MODELLING OF CROSSLINKED POLYURETHANE SYSTEMS

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by

SANJIB MALL

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CERTIFICATE

This is to certify that the work 'Modelling of Crosslinked Polyurethane Systems' has been carried out by Sanjib Mall under my supersvision and has not been submitted elsewhere for a degree.

7, August, 1982.

Dr.K.S.Gandhi
Professor
Department of Chem.Engg.
Indian Institute of
Technology,Kanpur-208016,
India

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-Sanjib Mall

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NOMENCLATURE

Letter Symbols

A	Isocyanate group
B	Hydroxyl group
C	Hydrogen of water molecule
D	Amino group
E	Urethane bond
$E(A)$	Expectation of event A
F	Urea bond
k	Reaction rate constant
M	Allophanate
M_c	Molecular weight between branch points
M_w	Molecular weight of polymer
N	Biuret
$P(A)$	Probability of event A
R	Ratio of A group concentration to B group concentration
t	Time
w_s	Sol fraction

Greek Symbols

α	Conversion of A groups
β	Conversion of B groups
γ	Conversion of C groups
δ	Conversion of D groups
ϵ	Conversion of E groups
ϕ	Conversion of F groups

Greek Symbols

ρ Ratio of Polyfunctional hydroxyls to all active hydrogens

θ Dimensionless time

Subscripts

$A, B, \ldots, N$ Pertaining to the respective groups (functional)

$1, 2$ Pertaining to structural asymmetry of NCO and OH

o Initial condition

Superscripts

$*$ Pertaining to structural asymmetry

r Monomeric group

$-$ Average

ABSTRACT

Diisocyanates, as well as some triols, which are reactants for polyurethane systems, are known to exhibit unequal reactivity. Polyurethane network formation has been modelled in this work taking into account unequal reactivity due to the asymmetry and induced asymmetry of the functional groups in the monomers. Using the model developed, stoichiometric ratios of reactants leading to gelation in polyurethane systems have been calculated by employing a combination of kinetics of reactions and probabilistic methods. The effect of secondary reactions of allophanate and biuret formation was also evaluated. It was shown that unequal reactivity can explain the occurrence of a minimum in geltime below an isocyanate to hydroxyl ratio of 1.

Unequal reactivity models were also used to compute CO_2 evolution and average molecular weight for polyurethane foam systems. The agreement between observed and computed rates of CO_2 evolution was satisfactory qualitatively.

CHAPTER 1

INTRODUCTION

Polyurethanes are called the polymers of the 80's. This is because they have a wide range of useful properties and they have not been fully exploited yet. Presently new uses are being found and the annual consumption of this group of polymers is growing very fast. A look at the wide variety of uses of these polymers will explain this.

1. __Rigid Polyurethane Foams__ are used for construction, packaging, insulation, automobile bumpers and some special uses.

2. __Flexible Foams__ are used for cushions, packaging and some special uses.

3. Polyurethane Elastomers are used in extra strong automobile tyres, automobile fascia and shoe soles. The automobile industry found this polymer very attractive and analysts predict that in future the door panels and many of the car body parts are going to be made of polyurethanes.

The reasons for such usefulness are many

1) __Mechanical properties__ of the polyurethanes can be varied from soft elastomers to rigid character by simple alterations in the initial composition of reactants.

2) __Manufacturing time__ of the polyurethanes can be made very small as the reactions are very fast compared to other polymers even at ordinary temperatures. Infact by using some tin

catalysts the gelation time for the polymer can be brought down to as low as a few seconds.

3) Other product properties such as dimensional stability, flame retardation, oxidation resistance, color stability and other desirable properties can be imparted to polyurethanes by addition of a number of suitable additives.

4) Large energy savings in producing polyurethanes, can be effected by Reaction Injection Molding. This new technique of molding uses the fast nature of the polyurethane formation reaction. Such fast nature allows pumping of less viscous monomers into the mould where polymerization takes place in situ. Thus cost of melting and pumping of viscous polymer is avoided. The savings are considerable as calculations show[1] that petroleum equivalent a feedstock plus energy required for production is the least for Reaction Injection Molded polyurethane among all the synthetic matters including aluminium, steel and other mineral products.

Polyurethanes[2] are so named because the linking reaction between the reactive groups of the monomers (Hydroxyl and isocyanate) leads to the formation of urethane bonds as given below:

$$\sim\!\!OH + O = C = N \sim\!\!\sim \rightarrow \sim\!\!O - \overset{\overset{\displaystyle O}{\|}}{C} \!-\! \overset{\displaystyle H}{N} \sim\!\!\sim$$

(isocyanate)   (urethane)
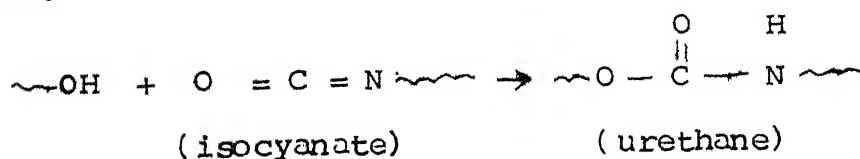
Usually bifunctional isocyanates are used, the most common ones being MDI (4,4' -Diphenylmethane-diisocyanate), TDI (Toluene diisocyanate) and HDI (Hexamethylene diisocyanate).

The hydroxyl compounds can be a mixture of diols and triols.
The diols are usually polyethers or polyesters terminated with
OH groups and are referred to as polyots. Besides the above
main reaction, many side reactions (including that with foaming
agents) also occur. The final properties of the crosslinked
polymer depend upon the extents to which all the reactions
took place and how they contributed to the formation of the gel.
Literature survey revealed some reaction models[3] and simulation[4]
but none which accounts for all the simultaneously occurring
reactions and their complex nature.

While it has been reported that diisocyanates exhibit
very complex unequal reactivity, only simple unequal reactivity
models[5] have been used in published works to model this system.
Moreover the complexities arising due to the presence of
reactive blowing agents have not been accounted for. The aim
of the present work is to account for these complexities and to
compare theoretical predictions with experimental data where
available.

The models presented in this work would be used in
Chapter 2 to predict the compositions leading to gel formation.
Crosslink density, urethane group concentration and solfraction
equations can be found in Appendix C. Such predictions are
useful in calculating the mechanical properties of the
polyurethanes.

In many applications, the gelled polymer is taken
out of the mold and further cured[6] using secondary reactions

(allophanate and biuret formation). The effect of these side reactions is studied in Chapter 3.

The models have been used to predict gel times and were checked with available experimental data. These results are contained in Chapter 4.

For the production of foams it is necessary that the CO_2 evolves at the right time when the polyurethane has gained sufficient viscosity. The viscosity is dependent on the average molecular weight. Hence it is necessary to look at the CO_2 evolution rate as well as the molecular weight of the reaction mixture as a function of time. These calculations are contained in Chapter 5.

A typical network forming polyurethane foam system has as initial reactants, a triol (B—$\overset{B}{\mid}$—B), a diol (B-B), a diisocyanate (A-A) and water as blowing agent (C-C). From among these the isocyanates and water exhibit unequal reactivity. Three basic types of unequal reactivity have been identified. Structural asymmetry[7] or asymmetry[8] refers to the situation where the different functional groups which are chemically similar react at different rates. Those cases where the reactivities of all the functional groups of a monomer are equal but different from that of the very same functional groups present at the end of a polymer chain have been termed induced asymmetry[8] or first shell substitution effects[9]. Cyclic monomers[8] which generate a chemically equivalent group after reaction constitute the last category of unequal reactivity. It is possible that a monomer may simultaneously possess one or more of the basic unequal reactivity characteristics. Several isocyanate monomers show the simultaneous presence of structural asymmetry and first shell substitution effect[2,10,11], while hydroxyl containing compounds may exhibit structural asymmetry.

BASIC REACTIONS:

In polyurethane systems the reaction between hydroxyl group and isocyanate group produces the urethane linkage:

$$\sim\!\!\sim\!N = C = O + HO\sim\!\!\sim \longrightarrow \sim\!\!\sim\!\overset{H}{\underset{\mid}{N}} - \overset{O}{\underset{\parallel}{C}} - O\sim\!\!\sim \tag{1}$$

The reactions between water and isocyanate group are:

$$N = C = O + H_2O \rightarrow \sim\sim N-\overset{H}{\underset{}{}}\overset{O}{\underset{}{C}}-OH \qquad (2a)$$

$$\sim\sim \overset{H}{N} - \overset{O}{C} - OH \longrightarrow \sim\sim NH_2 + CO_2 \qquad (2b)$$
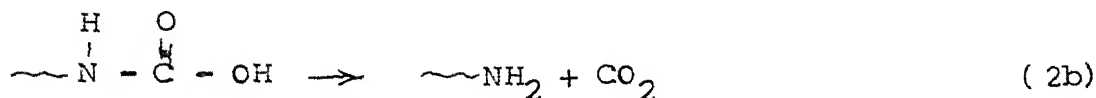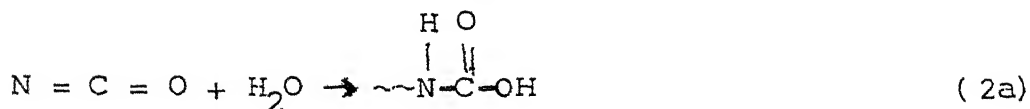
The gaseous CO_2 so liberated in the second reaction acts as the foaming agent. The amine generated in the second reaction can react with isocyanate group producing polyurea linkages:

$$\sim\sim N = C = O + H_2N\sim\sim \rightarrow \sim N - \overset{O}{C} - \overset{H}{N}\sim\sim \qquad (3)$$
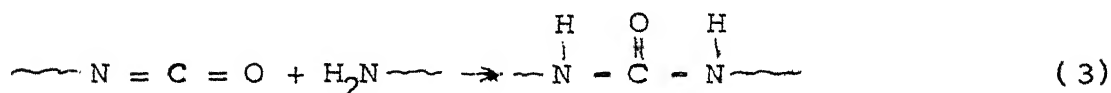
Apart from these, allophanate and biuret formation reactions can contribute to the chain branching. While some catalyst systems may promote these side reactions, generally their effect can be ignored except at high temperatures[2,6]. In the present chapter these side reactions will be assumed to be absent.

BASIC MODEL

Urethane Formation:

Let the diisocyanate monomers be denoted as A_1A_2 thereby explicitly recognizing that the two monomeric isocyanate groups will react at different rates. Let the diol be denoted by B_2 and the polyol by B_f. The same symbol B is being

assigned to all hydroxyl groups as all of them have been assumed
to be equally reactive. The structural asymmetry of the
diisocyanate monomer can be represented by the following
equations:

$$A_2A_1 + B \cdots \xrightarrow{k_1} {}^*A_2A_1B \cdots \tag{4}$$

$$A_1A_2 + B \cdots \xrightarrow{k_2} {}^*A_1A_2B \cdots \tag{5}$$
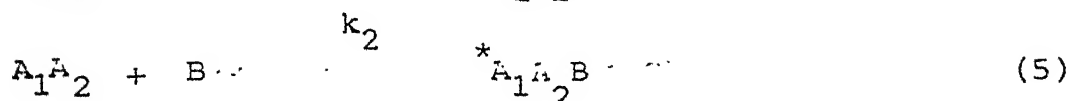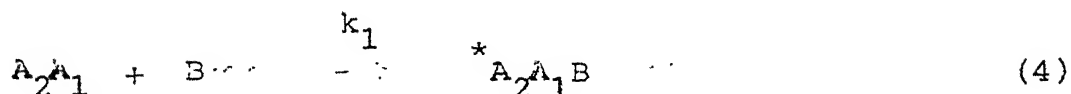
The A_1 and A_2 present at the end of a polymeric chain have been
clearly distinguished by putting a star as they will react
at a rate different from that of the corresponding monomeric
group due to first shell substitution effects. The first shell
substitution effect can be modelled as

$$\cdots A_2A_1^* + B \cdots \xrightarrow{k_1^*} \sim\sim A_2A_1B \cdots \tag{6}$$

$$\cdots A_1A_2^* + B \cdots \xrightarrow{k_2^*} \cdots A_1A_2B \cdots \tag{7}$$
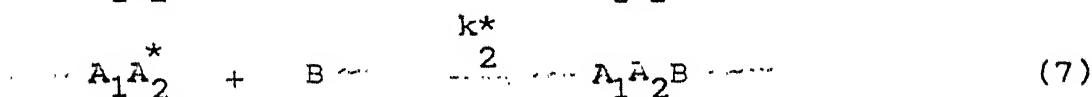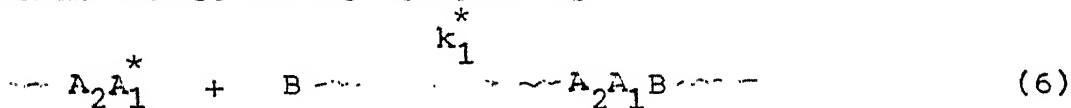
Linear polymerisation of such A_1A_2 monomer with only B_2 monomer
has been analysed by Gandhi and Babu[15] and their results can
be applied to analyse urethane formation by reactions (4) to
(7).

<u>Reactions with water:</u> Since reaction (2) is a very fast
one, it will be assumed to occur instantaneously. Then a water
molecule reacts with one isocyanate group and, in effect,
generates the amine group directly. The amine group can then
react with one isocyanate group by reaction (3). Such a
sequence of reactions is similar to those of a cyclic monomer
and in particular those between an anhydride and hydroxyl group.

In other words water can be modelled as a cyclic monomer. Let water be denoted by CD. The C group reacts first consuming one isocyanate group and generates a D group (amino group). The D group does not exist in the monomer and hence can not react till the "adjoining" C group reacts. Therefore the D group can be **present** only at the end of a chain while the C group cannotform the end of a chain. The D group can then react with one isocyanate group. The C and D groups can react with the isocyanate groups at different rates. For simplicity it will be assumed that the asymmetric characteristics of $A_1 A_2$ monomer are inherent to the $A_1 A_2$ monomer and the same characteristics used in urethane formation are applicable here also. In other words we are assuming that the relative reactivities of polymeric and monomeric A_1 and A_2 groups are unaltered irrespective of the group with which they react though their absolute reactivities may be different. The reactions with water may then be written as follows:

$$A_2 A_1 \;+\; CD \;\xrightarrow{\;Kk_1\;}\; {}^{*}A_2 A_1 CD \tag{8}$$

$$A_1 A_2 \;+\; CD \;\xrightarrow{\;Kk_2\;}\; {}^{*}A_1 A_2 CD \tag{9}$$
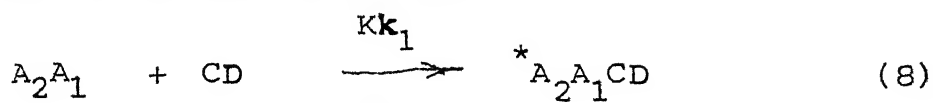
The A_1 and A_2 groups of the products of reactions (8) and (9) are polymeric in character. Thus we will write

$$A_2 A_1^{*} \;+\; CD \;\xrightarrow{\;Kk_1^{*}\;}\; {\sim}A_2 A_1^{*} CD \tag{10}$$

$$A_1 A_2^{*} \;+\; CD \;\xrightarrow{\;Kk_2^{*}\;}\; {\sim}A_1 A_2^{*} CD \tag{11}$$
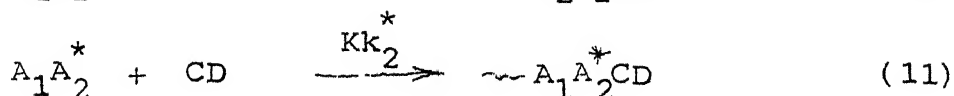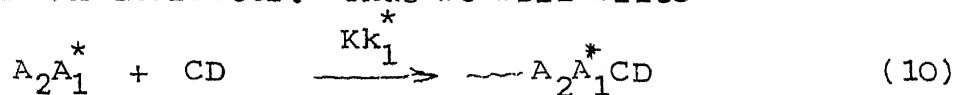
The D (amino) group reactions are

$$A_2 A_1 \;+\; D{\sim} \;\xrightarrow{\;K_R K\, k_1\;}\; {}^{*}A_2 A_1 \, D{\sim} \tag{12}$$

$$A_1A_2 + D \overset{K_R K\ k_2}{\longrightarrow} {}^*A_1A_2\ D \tag{13}$$

$$A_2{}^*A_1 + D \overset{K_R K\ k_1^*}{\longrightarrow} A_2A_1\ D \tag{14}$$

$$A_1{}^*A_2 + D \overset{K_R K\ k_2^*}{\longrightarrow} A_1A_2\ D \tag{15}$$
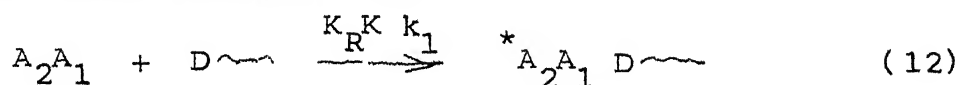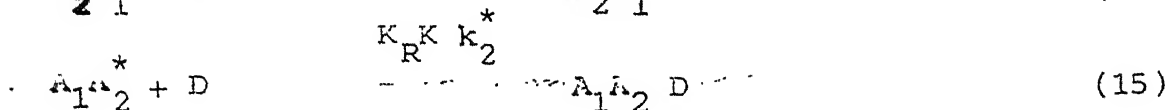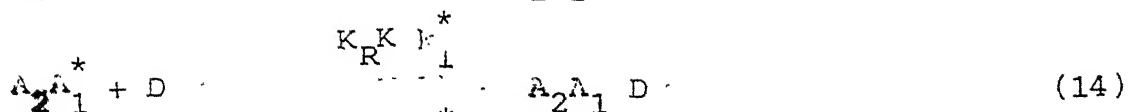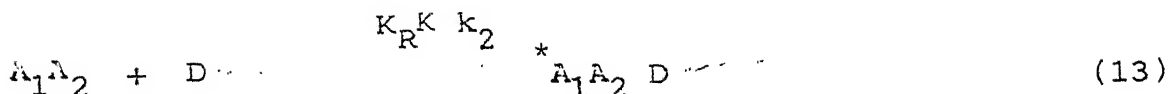
Reactions (4) to (15) then form the basic model of the system.

PROBABILITY OF NETWORK FORMATION

Initially let only monomers A_1A_2, B_2, B_f, CD be present. For the system being considered, gelation occurs through formation of structures like

```
  ··· B                                            B ···
  ··· B      B - A₁A₂CD...A₂A₁BB... A₁A₂ B⟨─B ···
   ·· B                                            B ···
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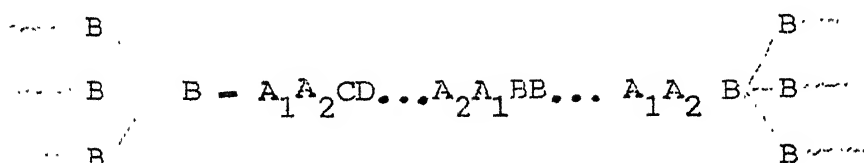
If the probability of occurrence of the above structure regardless of the number of intervening bifunctional CD and BB units, or the branching coefficient[16], can be calculated, the gel point can be predicted following Flory[16]. The probabilities of finding structures of the type

$$BA_1A_2-, \quad -A_1A_2CD-, \quad -A_1A_2BB-, \quad -A_1A_2B-$$
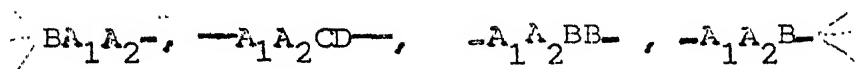
are needed to calculate the branching coefficient. All such probabilities have been shown[7-9,15] to be related to the fraction of the total number of the various groups that have been consumed in direct reaction. The probabilities and their interrelations can be calculated once the kinetics of the reactions is known. An example of such a calculation is given in Appendix A.

Probability of finding unreacted A_1A_2 monomer: This can be simply defined as the ratio of unreacted monomer concentrations at any given time and initially.

$$\alpha = A / [A]_o$$

Probabilities of reaction of A groups: During the course of reaction monomeric A_1 groups are lost by reaction (4) as well as by (5). Reaction (4) consumes a monomeric A_1 group by direct reaction whereas reaction (5) converts a monomeric A_1 group to a polymeric A_1 group. Let A_1^r be the moles of monomeric A_1 groups that have been consumed by reaction (4-15) per unit volume at any time. Following Gandhi and Babu[15] let us define the probability that a monomeric A_1 group has reacted as

$$\alpha_1 \equiv \frac{A_1^r}{[A] + A_1^r} \tag{16}$$

Such a definition has the advantage that it reaches a value of unity at the end of the reaction when A_1A_2 monomer is in stoichiometric deficiency. Similarly the probability that a monomeric A_2 group has reacted is

$$\alpha_2 \equiv \frac{A_2^r}{[A] + A_2^r} \tag{17}$$

Note that

$$[A]_o = [A] + A_1^r + A_2^r \tag{18}$$

When A_2^r moles of monomeric A_2 groups have reacted, the same number of polymeric A_1 or A_1^* groups have been created. IF $[A_1^*]$ is the concentration of unreacted polymeric A_1 groups at any time, then $A_2^r - [A_1^*]$ number of polymeric A_1^* groups have

react... to reaction (6). Hence, the probability of reaction of polymeric A_1 groups can be defined as

$$\gamma_1^* \equiv \frac{A_2^r - A_1^*}{A_2^r} \tag{19}$$

Similarly, the probability of reaction of polymeric A_2 groups is defined as

$$\gamma_2^* \equiv \frac{A_1^r - A_2^*}{A_1^r} \tag{20}$$

Probabilities of reaction of B groups: Let $[B_f]_o$ and $[B_2]_o$ represent the initial concentrations of the polyol and diol respectively. Let $[B]$ be the concentration of unreacted B ends present at any time. The probability that a randomly selected B group has reacted is defined as

$$\beta \equiv 1 - \frac{[B]}{f [B_f]_o + 2 [B_2]_o} \tag{21}$$

Probabilities of reaction of CD units: Let $[C]_o$ and $[C]$ respectively represent the concentrations of the CD monomer initially and at any time. Let D represent the concentration of unreacted D ends at any time. The number of CD units that have reacted per unit volume is $C_o - C$. Hence the probability of finding a CD unit where C group has reacted can be defined as

$$\gamma \equiv \frac{[C]_o - [C]}{[C]_o} \tag{22}$$

During the course of reaction, $[C]_o - [C]$ moles of CD monomer units have reacted and hence that many moles of D ends have been created per unit volume. Out of these only $[D]$ moles per unit

volume of unreacted D ends are present. Hence the moles per unit volume of CD units in which both C and D groups have reacted is equal to $C_o - C - D$. The probability of finding a CD unit where both C and D have reacted can be defined as

$$\delta \equiv \frac{C_o - C - D}{C_o} \tag{23}$$

Again note that β, γ and δ will attain unity at the end of the reaction if A_1A_2 monomer is in stoichiometric excess.

Stoichiometric relationship: The total number A groups that have reacted must be equal to the total number of B, C and D groups that have reacted. Hence

$$S \equiv A_1^r (1 + \alpha_2^*) + A_2^r (1 + \alpha_1^*) = f[B_f]_o + 2[B_2]_o \beta + [C]_o (\gamma + \delta)$$

In terms of the above defined probabilities, the first equality reduces to

$$S = \alpha_1 (1 - \alpha_2)(1 + \alpha_2^*) + \alpha_2(1 - \alpha_1)(1 + \alpha_1^*) A_o / (1 - \alpha_1)(1 - \alpha_2) \tag{24}$$

Let us define the fraction of polyfunctional groups, ρ,

$$\rho \equiv \frac{f[B_f]_o}{f[B_f]_o + 2[B_2]_o + 2[C]_o} \tag{25}$$

and fraction of hydroxyl groups contributed to the diol, d,

$$d \equiv \frac{2[B_2]_o}{f[B_f]_o + 2[B_2]_o} \tag{26}$$

and the fraction of blowing agent groups, b,

$$b \equiv \frac{2[C]_o}{f[B_f]_o + 2[B_2]_o + 2[C]_o} \tag{27}$$

The above three quantities are related through

$$\hat{F} = (1 - d)(1 - b) \text{ or } d(1 - b) = 1 - \hat{F} - d \qquad (28)$$

Further let R be defined the stoichiometric ratio, R, as the ratio of initial concentrations of A groups and the concentrations of all the groups with which A can react

$$R \equiv \frac{2[A]_o}{f[B_f]_o + 2[B_2]_o + 2[C]_o} \qquad (29)$$

Then using (25) to (29), the total B, C, D groups that have reacted, S, is given by

$$S = \frac{[A]_o}{R(1 - d)} \left[2\hat{F} + (1 - d - \hat{F})(\hat{F} + b) \right] \qquad (30)$$

Probability of a structure of the type $-A_1 A_2 BB-$:   The structure being considered can be formed in four ways:

(i) Monomeric A_1 group reacts, then the polymeric A_2 group reacts with a B_2 unit and the B end reacts subsequently. $-A_1 A_2^* BB-$ can represent such formation (ii) Monomeric A_2 group reacts, the polymeric A_1 group reacts with a B_2 unit and the B end reacts afterwards. $-A_2 A_1^* BB-$ represents this type of formation (iii) One B group of a B_2 unit can react, the other B end can then react with monomeric A_1 group and the polymeric A_2 group can react thereafter. $-A_2 A_1^* BB-$ symbolises this type of formation (read from right to left). (iv) A B_2 unit can react, monomeric A_2 reacts with the other B end and then polymeric A_1 group reacts. $-A_1^* A_2 BB-$ is the representation of this type of formation. The total probability of formation of $-A_1 A_2 BB-$ type of unit, irrespective of the internal arrangements of $A_1 A_2$ or the ways in which the unit was formed, is the sum of the probabilities

of occurrence of the four types of sequences of events listed above.

The probability of occurrence of the first of the above sequences will be calculated as an example. The probability is given by

$$\begin{pmatrix}\text{probability of finding}\\ \text{a monomeric } A_1 \text{ reacted}\\ \text{group next to a bond}\end{pmatrix} \begin{pmatrix}\text{probability that}\\ \text{polymeric } A_2 \text{ reacts}\\ \text{with a BB unit}\end{pmatrix} \begin{pmatrix}\text{probability that}\\ \text{the B end has}\\ \text{reacted}\end{pmatrix}$$

$$= \left(\frac{A_1^r}{s}\right) \left(\alpha_2^* \quad \frac{2[B_2]o^\beta}{s}\right) (\beta)$$

Similarly the probability of the second, third and fourth sequences can be calculated to be, respectively,

$$\frac{A_2^r}{s} \cdot \alpha_1^* \quad \frac{2[B_2]o^\beta}{s} \cdot \beta \; , \quad \frac{2[B_2]o^\beta}{s} \cdot \gamma \; \frac{A_1^r}{s} \cdot \alpha_2^* , \quad \frac{2[B_2]o^\beta}{s} \cdot \beta \frac{A_2^r}{s} \cdot \alpha_1^*$$

Hence the total probability of finding $-A_1A_2BB-$ unit P_{BB} is given by

$$P_{BB} = 2 \; \frac{A_1^r \alpha_2^* + A_2^r \alpha_1^*}{s} \cdot \frac{2[B_2]o}{s} \beta^2$$

After substitution of (24) and (30)

$$P_{BB} = 4 \; \frac{\alpha_1 \alpha_2 (1-\alpha_2) + \alpha_2 \alpha_1(1-\alpha_1)}{\alpha_1(1-\alpha_2)(1+\alpha_2^*) + \alpha_2(1-\alpha_1)(1+\alpha_1^*)} \cdot \frac{d \beta^2}{2\beta o + (1-d-\beta)(\gamma+\delta)}$$

(31)

<u>Probability of a structure of the type $-A_1A_2CD-$</u> : Analysing in a manner similar to the previous section, there are eight ways in which the structure being considered can form. Using a notation similar to the earlier section these eight ways can be listed as: $-A_1A_2^*CD-$, $-A_1A_2^*DC-$, $-A_2A_1^*CD-$, $-A_2A_1^*DC-$, $A_1^*A_2CD-$, $-A_1^*A_2DC-$, $-A_2^*A_1CD-$, $-A_2^*A_1DC-$. As an example, the fifth structure may be interpreted to have formed when a monomeric A_2

group reacts with CD monomer and subsequently the polymeric A_1 group and D group generated react. Following the method employed in the earlier section, the probabilities of the above eight structures can be calculated and are given by $\frac{A_1^r}{s} \cdot \alpha_2^* \cdot \frac{C_0\delta}{s}$, $\frac{A_1^r}{s} \cdot \alpha_2^* \cdot \frac{C_0\delta}{s}$, $\frac{A_2^r}{s} \cdot \alpha_1^* \cdot \frac{C_0\delta}{s}$, $\frac{A_2^r}{s} \cdot \alpha_1^* \cdot \frac{C_0\delta}{s}$, $\frac{C_0\delta}{s} \cdot \frac{A_2^r}{s} \cdot \alpha_1^* \cdot \frac{C_0\delta}{s}$, $\frac{A_1^r}{s} \alpha_2^*$, $\frac{C_0\delta}{s} \cdot \frac{A_1^r}{s} \alpha_2^*$ respectively. The total probability of finding $-A_1A_2CD-$ structure irrespective of the internal arrangements of the A_1A_2 and CD units P_{CD} is then the sum of all the above eight probabilities or

$$P_{CD} = 4 \frac{A_1^r \alpha_2^* + A_2^r \alpha_1^*}{s} \cdot \frac{C_0\delta}{s}$$

In terms of probabilities and other definitions adopted earlier

$$P_{CD} = 4\frac{\alpha_1 \alpha_2^*(1-\alpha_2) + \alpha_2\alpha_1^*(1-\alpha_1)}{\alpha_1(1-\alpha_2)(1+\alpha_2^*) + \alpha_2(1-\alpha_1)(1+\alpha_1^*)} \cdot \frac{(1-d-\beta)\delta}{2\beta + (1-c-\beta)(\gamma+\delta)}$$

(32)

Probability of a structure of the type $-A_1A_2B-$: There are four ways in which this structure can form:

$$-A_1A_2^* B \;, \quad -A_2A_1^* \;, \quad -A_1^*A_2B \;, \quad -A_2^*A_1B$$
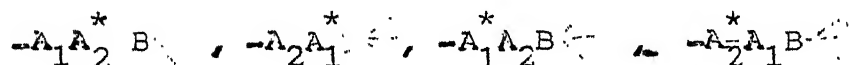
The probabilities of these four structures respectively are:

$$\frac{A_1^r}{s} \cdot \alpha_2^* \cdot \frac{f B_f o\beta}{s} \;, \quad \frac{A_2^r}{s} \cdot \alpha_1^* \cdot \frac{f B_f o\beta}{s} \;,$$

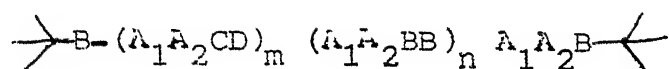$$\frac{f B_f o\beta}{s} \cdot \frac{A_2^r}{s} \cdot \alpha_1^* \;, \quad \frac{f B_f o\beta}{s} \cdot \frac{A_1^r}{s} \cdot \alpha_2^*.$$ The total probability of finding this structure P_{B_f} is given by

$$P_{B_f} = 2 \frac{A_1^r \alpha_2^* + A_2^r \alpha_1^*}{s} \cdot \frac{f B_f o\beta}{s}$$

and after substitution of earlier definitions

$$P_{B_f} = 4 \frac{\alpha_1 \alpha_2^*(1-\alpha_2) + \alpha_2 \alpha_1^*(1-\alpha_1)}{\alpha_1(1-\alpha_2)(1+\alpha_2^*) + \alpha_2(1-\alpha_1)(1+\alpha_1^*)} \cdot \frac{\rho(1-d)\beta}{2f\beta + (1-d-\rho)(\gamma+\delta)}$$

(33)

Branching Coefficient: Consider the following structure

$$\rightarrow B-(A_1 A_2 CD)_m \ (A_1 A_2 BB)_n \ A_1 A_2 B \leftarrow$$

The probability of the above structure is simply given by

$$\beta \cdot (P_{CD})^m (P_{BB})^n \cdot P_{B_f}$$

However the $-A_1 A_2 CD-$ and $-A_1 A_2 BB-$ units can be interchanged and it will lead to $(m+n)!/(m!n!)$ number of structures with the same probability. Hence the total probability of finding such a structure irrespective of the internal rearrangements is

$$\frac{(m+n)!}{m! \ n!} \quad P_{B_f}(P_{CD})^m \ (P_{BB})^n$$

Branching coefficient is equal to the probability that a B group selected at random from one of the B_f units will lead to a B group of another B_f unit regardlessof the number of connecting bifunctional units. Thus branching coefficient is given by

$$\sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \beta \, P_{B_f} \frac{(m+n)!}{m! \ n!} (P_{CD})^m (P_{BB})^n \quad \text{or}$$

$$\frac{\beta \, P_{B_f}}{1 - P_{CD} - P_{BB}}$$

Following arguments of Flory[13], the gel point occurs when

$$(f-1) \frac{\beta \, P_{B_f}}{1 - P_{CD} - P_{BB}} \geqslant 1$$

(34)

The above criteria along with kinetics of the reactions can be used to predict the fractional conversions at which gelation

will occur. The inter-relations between probabilities have been derived in Appendix I assuming second order kinetics. The gel criteria then simplifies to

$$(f-1)\frac{4\beta^2 f(\alpha_2^* + K_A\alpha_1^*)(1-d)}{\left[1+\alpha_2^* +K_A(1+\alpha_1^*)\right]\left[2f\beta+(1-d-f)(\gamma+\delta)\right]-4(\alpha_2^*+K_A\alpha_1^*)\left[(1-d-f)+fd\beta^2\right]} \geq 1$$

(35)

The above criteria must be simultaneously satisfied along with the stoichiometric relation which now reduces to

$$\frac{\alpha_1}{1+K_A\alpha_1}\left[1+\alpha_2^* + K_A(1+\alpha_1^*)\right]= \frac{1}{R(1-d)}\left[2f\beta +(1-d-f)(\gamma+\delta)\right]$$

(36)

Both these equations are proved in the appendix I.

RESULTS AND DISCUSSION

The gelation criteria given by (34) can be used to predict whether a particular initial composition specified by R, f and d will lead to the formation of an infinite network or not. Further if a gel were to form, the fractional decrease in the initial functional group concentrations required before gelation can occur can also be predicted by (34). Results have been obtained in this chapter/for reaction of a diisocyanate with a triol (f = 3), a diol and water.

Recovery of appropriate limits: Under appropriate restrictions, the present model must reduce to those developed by earlier workers. A few such examples are given to demonstrate the validity of the present model. The kinetics presented in the

Appendix I will be used as and when necessary.

(i) Limit of equal reactivity: When $k_2/k_1 \equiv K_A = 1$, $k_1^*/k_1 \equiv K_1 = 1$ and $k_2^*/k_2 \equiv K_2 = 1$, both the functional groups, A_1 and A_2, are equally reactive in their monomeric as well as polymeric form. Further if $K = 2$ and $K_R = 0.5$, the CD monomer behaves like B_2 monomer[6]. Flory's[13] equal reactivity limit must be recovered with these restrictions. The following relationships can be easily established from the appendix with the above restrictions:

$$\gamma = 2\beta - \beta^2, \ \delta = \beta^2, \ \alpha_1 = \alpha_2, \ \alpha_1^* = \alpha_2^*, \ 1 - \alpha_1^* = -\frac{1+\alpha_1}{\alpha_1}\left[\frac{1-\alpha_1}{1+\alpha_1} - \sqrt{\frac{1-\alpha_1}{1+\alpha_1}}\right]$$

(37)

If p_A is defined as the fraction of total A groups that have reacted, then

$$p_A = \frac{A_1^r(1+\alpha_2^*) + A_2^r(1+\alpha_1^*)}{2\,[A]_o} = \frac{\alpha_1}{1+\alpha_1}(1 + \alpha_2^*)$$

(38)

From (37) and (38), it can be shown that

$$\frac{\alpha_1}{1+\alpha_1} = \frac{p_A(2 - p_A)}{2} \quad \text{and} \quad \alpha_1^* = \frac{p_A}{2-p_A}$$

Similarly if p_B is defined as the fraction of B, C and D groups that have reacted, then, it can be shown that

$$p_B = \frac{\{f[B_f]_o + 2[B_2]_o\}\beta + [C]_o(\gamma + \delta)}{f[B_f]_o + 2[B_2]_o + 2[C]_o} = \beta$$

(39)

If all the above results are substituted in the stoichiometric relationship (36), it reduces to $R\,p_A = p_B$ and the gelation criteria (35) reduces to

$$(f-1) \frac{j \; p_A \; p_B}{(1-(1-j) \; p_A p_B)} > 1 \qquad\qquad (40)$$

Both these results are identical to that given by Flory[16]. Note that Flory's r is 1/R and BB monomer in Flory's reference is the AA monomer of this paper.

(ii) Limit of only first shell substitution effect: This limit is obtained when $K_A = 1$, $K_1 = K_2$. To make CD equivalent to B_2, we let K = 2 and $K_R = 0.5$. Hence $\alpha_1 = \alpha_2$, $\alpha_1^* = \alpha_2^*$, $= 2\beta - \beta^2$, $= \beta^2$. Miller and Macosko[8] considered gelation of A_g with B_2 where A_g exhibits first shell substitution effect. To compare therefore we have to put g = 2 in their results and f = 2, β = 1, d = 0, b = 0 in ours. Miller and Macosko[8] define p_i to be the fraction of the initial A_g units in which i number of A groups have reacted. It is easy to show that

$$p_0 = \frac{[A]}{[A]_0} = \frac{1-\alpha_1}{1+\alpha_1} \;, \quad p_1 = \frac{2[A_1^*]}{[A]_0} = \frac{2\alpha_1(1-\alpha_2^*)}{1+\alpha_1} \text{ and}$$

$$p_2 = \frac{2 A_1^r \alpha_2^*}{[A]_0} = \frac{2\alpha_1\alpha_2^*}{1+\alpha_1} \;.$$ If these results are substituted in the gel criteria given by Miller and Macosko, it reduces to $2 R \alpha_1 \alpha_2^* / (1 + \alpha_1) = 1$. For the case being considered, the stoichiometric relation (36) simplifies to $R\alpha_1(1 + \alpha_2^*)/(1 + \alpha_1) = \beta$ and the gel criteria (35) is given by $2\beta\alpha_2^*/(1 + \alpha_2^*) = 1$. When these two are combined the gel criteria is identical to that given by Miller and Macosko[5]

Bokare and Gandhi[12] considered the crosslinking of f functional epoxide with g/2 functional primary amine, where the amine hydrogens exhibit first shell substitution effect. They also considered the side reaction of the epoxide group with the

secondary hydroxyl group generated. If the hydroxyl group is considered to be nonreactive and if $g = 2$, their results are for the reaction between A_1A_2 with B_f where A_1A_2 has only first shell substitution effect. As hydroxyl groups are not reactive only secondary amine S_1 and tertiary amine T_2 (defined in reference 9) exist and gel criteria given by them[12] reduces to $2(f-1) T_2/e_o = 1$. T_2 is the number of tertiary amine units or in our notation, A_1A_2 units in which both A_1 and A_2 have reacted. Hence,

$$\frac{T_2}{e_o} = \frac{2 A_1^r \alpha_2^*}{f B_f} = R \frac{\alpha_1 \alpha_2^*}{1 + \alpha_1}$$

and gel criteria given in equivalent to $2(f-1) R\alpha_1\alpha_2^*/(1 + \alpha_1) = 1$. This is identical to that predicted by (35) and (36). Note $d = b = 0$ since the reaction is between A_1A_2 and B_f only.

(iii) Limit of only structural asymmetry: This limit is obtained when $K_1 = K_2 = 1$, $K = 2$, $K_R = 0.5$. Hence $\alpha_1^* = \alpha_2^*$, $\gamma = 2 - \alpha^2$, $b = \alpha^2$. For this case Miller and Macosko[5] have given the gelation criteria to be $r = q_1 q_2 [1 + (f-2)a_f]$. q_1 and q_2 are the fraction of A_1 and A_2 groups consumed and are easily, shown to be given by $\alpha_1 (1 + K_A\alpha_1^*)/(1 + K_A\alpha_1)$ and $\alpha_1 (K_A + \alpha_2^*)/(1 + K_A\alpha_1)$ respectively. Noting that $r = 1/R$ and $a_f = \rho$, the gelation criteria of Miller and Macosko reduces to $R\alpha_1\alpha_1^* (K_A + 1) [1 + (f-2)\rho]/(1 + K_A\alpha_1) = 1$. Simplifying (35) and (36) it can be shown that (35) is identical with that of Miller and Macosko.

Gelation Envelope: For a given system, the reaction rate constants are fixed and (35) can predict the fractional conversions at

which gelation will occur once R, ρ and d are specified.
However, the maximum possible conversion is complete conversion
of those groups which are in stoichiometric deficiency. For
example when $R < 1$, gel can form only when all $\alpha \leq 1$. Hence for
a given ρ and d, by gelation condition and stoichiometry,
there exists a R_{min}, a minimum value of stoichiometric ratio,
at which gelation can occur when all $\alpha = 1$. For any $R < R_{min}$,
gelation is not possible for the same value of ρ and d because,
before the required amounts of polyfunctional B groups can
react A_1A_2 monomer would be exhausted. Similarly there
will be a R_{max} such that for $R > R_{max}$, gelation will not occur.
To illustrate this point consider as an example gelation of AA
with B_3 and B_2. The system is one of equal reactivity and
$d = (1 - \rho)$ since b = 0. The gel criteria has been shown to be

$$\frac{2 \rho\, p_A\, p_B}{1 - (1-\rho)\, p_A p_B} \geq 1 \qquad (40)$$

and the stoichiometric equation is given by $Rp_A = p_B$. For $R < 1$,
the maximum value p_A can attain is 1 while p_B is always less
than 1. Using stoichiometry, the gelation criteria simplifies
to

$$\frac{2 \rho R\, p_A^2}{1 - (1-\rho)\, Rp_A^2} \geq 1 \quad \text{or} \quad R \geq \frac{1}{p_A^2\, (1 + \rho)}$$

Thus when $p_A = 1$, R takes its minimum possible value:
$R_{min} = 1/(1 + \rho)$. Clearly gelation can not occur at the same
if $R < R_{min}$ since that would require $p_A > 1$. If $R > R_{min}$ gelation
can occur but for $p_A < 1$. Similarly if $R > 1$, the maximum
value possible for p_B is 1 while $p_A < 1$. Now the gelation criteria
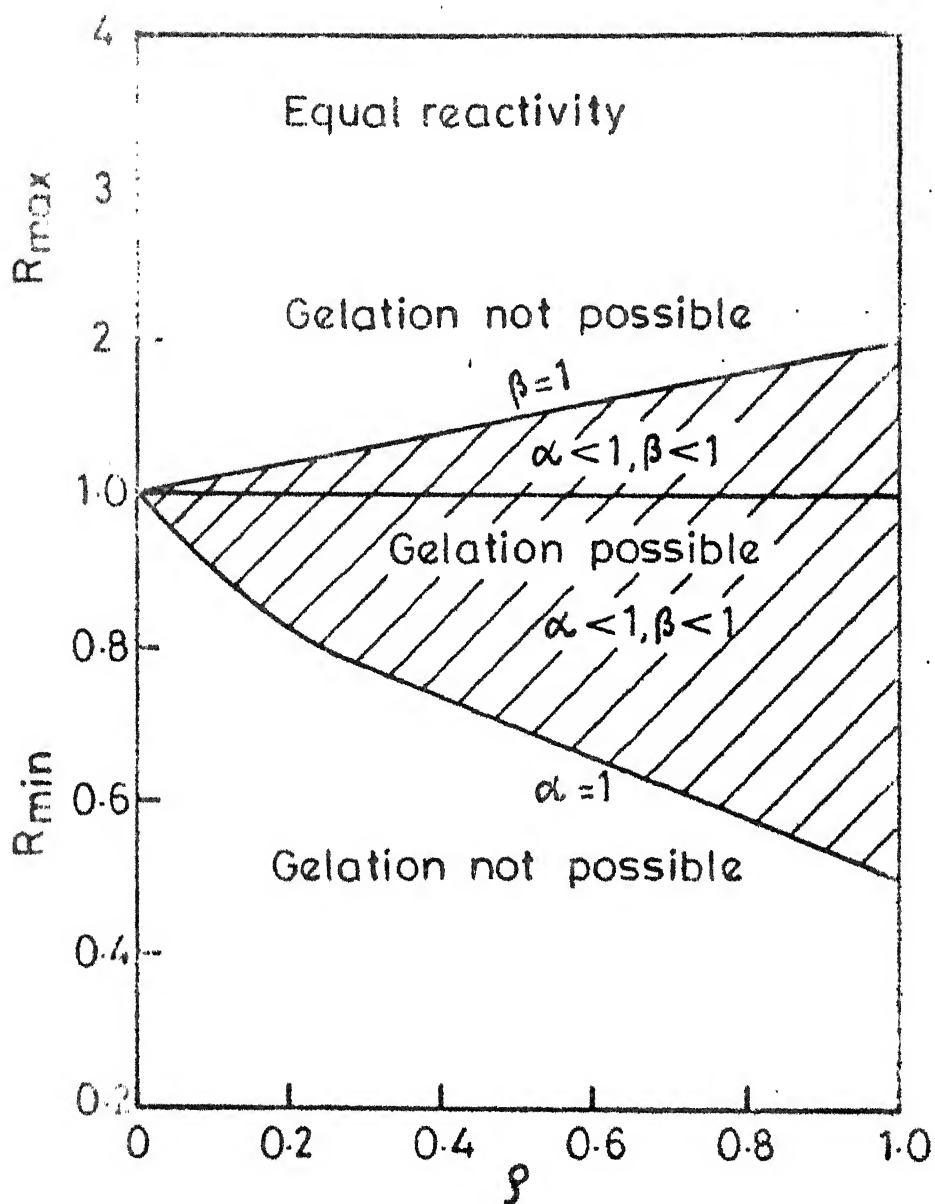will reduce to

FIGURE 1 :   Gelation envelope for the case of equal
             reactivity. ($K=2$, $K_R=1/2$, $K_A=K_1=K_2=1$)

$$\frac{2 \, p_B^2}{(R - (1 - \omega) \, p_B^2)} \geqslant 1 \quad \text{or} \quad R \geqslant (1 + \rho) \, p_B^2$$

Hence the maximum value of the stoichiometric ratio, R_{max}, at which gelation can occur is given by $(1 + \rho)$ when p_B has been equated to one. Gels will form only if $R \leqslant R_{max}$ and for $R \leqslant R_{max}$, $p_B \geqslant 1$ at the gel point. Thus gelation is possible only if $R_{min} \leqslant R \leqslant R_{max}$ for a given Γ. These two limits then define the boundaries of the gelation envelope and it is shown in figure 1 for equal reactivity case. Gelation will occur only if the initial composition falls inside the envelope. The R_{min} vs. Γ and R_{max} vs. Γ will be referred to as the lower and upper boundaries of the envelope respectively. The gelation envelopes for different parametric values of the reaction rate constants and d will be presented in this section. First to be considered is the case when $d = 0$ for simplicity.

Gelation envelope in the absence of bifunctional monomer:

    (i) R_{min} versus ρ : This gives the lower boundary of the gelation envelope. R_{min} would be less than unity and therefore $A_1 A_2$ monomer is in stoichiometric deficiency. The value of R_{min} is obtained when all A groups have been consumed or when $\varkappa_1 = \varkappa_2 = \alpha_1^* = \alpha_2^* = 1$. Then (35) reduces to

$$\frac{4 \beta^2 \rho}{2 \rho \beta + (1 - \rho)(\gamma - \delta)} \geqslant 1 \quad \text{or} \quad \rho \left[4 \beta^2 - 2 \rho \beta + (\gamma - \delta) \right] \geqslant (\gamma - \delta)$$

$$\tag{41}$$

and (36) reduces to

$$2R = 2 \rho \beta + (1 - \rho)(\gamma + \delta) \tag{42}$$

In the above we have taken $f = 3$ and $d = 0$. By definition $\gamma - \xi$ is always positive and $0 \leq \rho \leq 1$. Then (41) can be rearranged to get

$$\rho(4\xi^2 - 2\xi) \geq (1-\rho)(\gamma - \xi)$$

and hence the minimum value that ξ must attain before gelation can occur is given by

$$4\xi^2 - 2\xi \geq 0 \quad \text{or} \quad \xi \geq 0.5$$

Further note that gelation will occur at $\xi = 0.5$ if $\rho = 1$ regardless of the values of the reaction rate constants. The value of R_{min} at $\rho = 1$ therefore is obtained from (42) to be 0.5 and this result is common to all gelation envelopes.

If gelation were to occur at $\beta = 1$ and since $\beta = 1$ also means that $\gamma = \delta = 1$, the only value possible for R_{min} is unity by (42). Conversely when $R_{min} = 1$, $\beta = \gamma = \xi = 1$ and any value of $\rho > 0$ will lead to gelation by (41). But when $\rho = 0$ only $R_{min} = 1$ will satisfy (41) and (42). Therefore, $R_{min} = 1$ when $\rho = 0$ forms a common point for all gelation envelopes.

Since A_1A_2 monomer is completely consumed, only the time required for gelation and not the lower boundary of the gelation envelope is affected by the reaction rate constants' ratios K_A, K_1 and K_2. Only the reactivity ratios K and K_R, which describe the effect of the behaviour of the blowing agent, influence the results.

Effect of K: This parameter indicates the effect of the relative reactivity of the C group. Let the two obvious limits given by $K = 0$ and $K \to \infty$ be considered. When $K = 0$, the blowing agent is nonreactive and hence acts simply as a

diluent. Both γ and δ are therefore zero and (41) predicts that gelation will occur as soon as β reaches 0.5 and hence by (42), $R_{min} = \rho/2$. This result indicates that as ρ is increased, more AA monomer required for gelation. It is an expected result since as ρ is increased, the fraction of the reactive B_f monomer increases while the fraction of nonreactive blowing agent decreases. As $K \rightarrow \infty$ the blowing agent CD reacts instantaneously and completely before any B groups can be consumed. Hence $\gamma = \delta = 1$ and therefore gelation will again occur as soon as $\beta = 0.5$. By (42) therefore $R_{min} = 1 - 0.5\rho$. Firstly this result shows that for the same value of ρ, R_{min} required for $K = 0$ is less than that for $K \rightarrow \infty$. This is to be expected since CD does not consume any A_1A_2 when $K = 0$ while CD requires stoichiometrically equivalent of A_1A_2 when $K \rightarrow \infty$. Secondly the above result shows that, unlike when $K = 0$, as ρ is increased, A_1A_2 required for gelation decreases. This can be understood since CD monomer consumes A_1A_2 monomer at the beginning itself forming —AACD— type prepolymer but not resulting in crosslinking. Hence as ρ is increased, the CD monomer fraction decreases and thus the requirement of A_1A_2 is reduced.

The blowing agent can therefore act in two opposing ways: as a nonreactive diluent and as a chain extending consumer of AA. As ρ is increased, the former effect tends to increase R_{min} while latter effect tends to decrease R_{min}. The values of K and ρ determine the effect that dominates. It is pertinent here to point out that, had CD been assumed to be equally reactive as B_f, the theory would predict a monotonic decrease in R_{min} as ρ is

increased. Numerical results illustrating the effect of K are presented in figure 2 for $K_R = 1$. For $K \gg ?$, the diluent effect is not there at all and R_{min} monotonically decreases with increasing r. However when K is sufficiently low, such as 0.1, very interesting behaviour that reflects a balance of the two effects already described is observed. At such a low value of K, the blowing agent reacts very slowly and should behave like a diluent. But at low values of ρ, large amounts of CD are present and thus the low reactivity is compensated for by the high concentration. As a result, a significant amount of AA is consumed in chain extension. Hence at low values of ρ, the blowing agent behaves like a chain extending agent and increased values of ρ cause a decrease in R_{min}. However at sufficiently high values of ρ, large amounts of fast reacting B groups are present to consume AA monomer leaving the blowing agent essentially unreacted. The blowing agent now essentially plays the role of a diluent and hence increased ρ results in an increased R_{min}. This conclusion is confirms by calculations which show that $\gamma \cong \xi \cong 0$ in curve 2 till the minima is reached. To the left of the left boundary of this curve, gelation will not take place since too few B_3 molecules are there to create sufficient number of connected branch points. No gelation is possible to the right of the right boundary since excess of B_3 monomer is present leading to too many unconnected B groups.

All the curves of figure 2 indicates, as expected, that at constant ρ an increased value of K would mean more consumption of AA by CD or larger chain lengths between branch points and hence increased R_{min}. Another conclusion that can be drawn from these
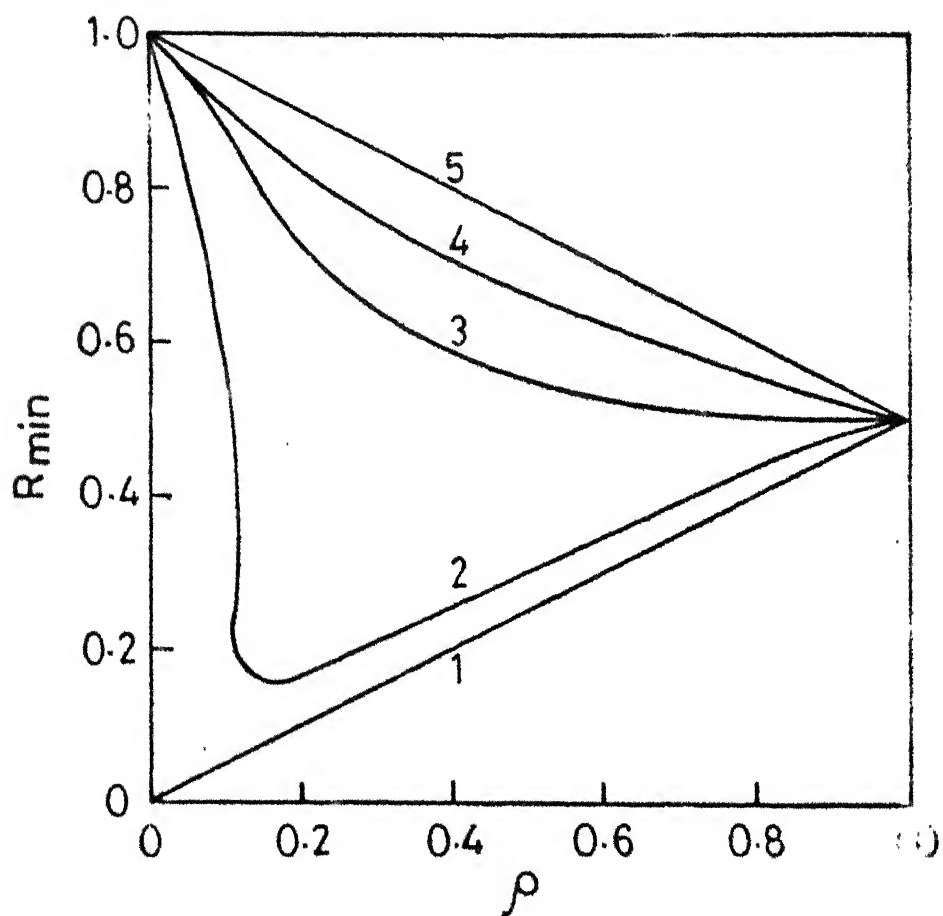
FIGURE 2 : Effect of K on R_{min}. The curves 1-5 are for K=0, 0.1, 1, 2 and ∞ respectively with K_R =1

curve is that, if R is fixed, gels can be formed even if large amounts of blowing agent are added if a retarding agent for its reaction is found.

Effect of K_R: Again, it will be fruitful to investigate the two limits of $K_R = 0$ and $K_R \to \alpha$. When $K_R = 0$, the D group is unreactive and hence CD acts like a monofunctional blocking agent and $= 0$. The gel criteria now reduces to

$$ \rho \geqslant \frac{R_{min}}{2 \, \rho^2} \tag{43} $$

and stoichiometric relation is given by

$$ 2R = 2 \rho + (1 - \rho) \gamma \tag{44} $$

When $\beta = 1$, γ is also equal to unity and $R = 1 + 0.5 \rho$ by (44). We can therefore infer from (43) that gelation will occur only if $\rho \geqslant 1/3$. This is shown in figure 3 in curve 1. The top portion of curve 1 was obtained for $\alpha < 1$ and $\beta < 1$ for the indicated values of the parameters. The relations (43) and (44) can not be combined into one analytical expression and numerical results can be presented only after assuming a value for K. The portion of the curve 1 for $1/3 \leqslant \rho \leqslant 1$ has been calculated for $K = 2$. As ρ is increased, the fraction of blowing agent is decreased and the amount of AA monomer wastefully consumed and blocked decreases. Thus R_{min} decreases as ρ is increased as seen in figure 3.

When $K_R \to \alpha$ the D group reacts instantaneously or in effect each C group that reacts consumes two A groups. Thus $\gamma = \delta$ and therefore gelation occurs as soon as $\beta = 0.5$. Stoichiometry requires that
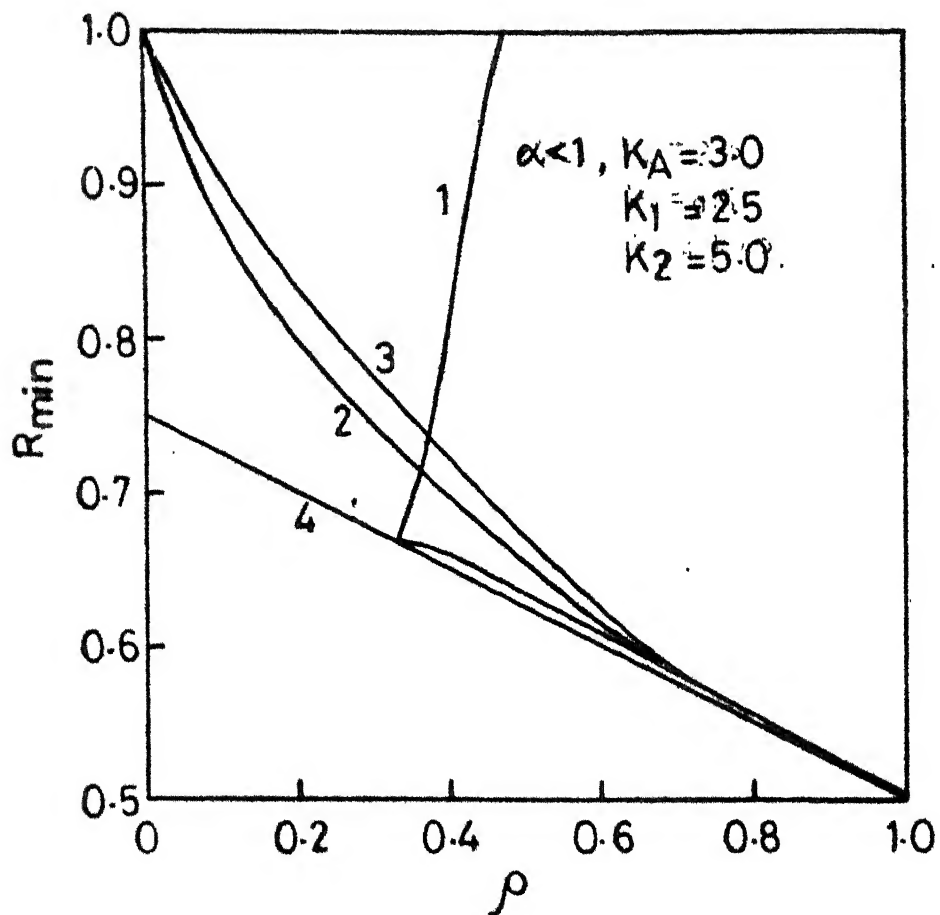
FIGURE 3 : Effect of K_R on R_{min}. Curves 1-4 are for K_R =0,0,1, 0.5 and ∞ respectively with K=2

$$R = \beta + (1 - \beta)\gamma = \beta + (1 - \beta)\left[1 - (1 - \beta)^K\right]$$

and therefore

$$R_{min} = \frac{1}{2} + (1 - \beta)\left[1 - \left(\frac{1}{2}\right)^K\right]$$

Results of this limit are represented by curve 4 of figure 3
for $K = 2$. Note that at $\beta = 0$, $\beta = 0.5$ is a meaningless
criteria and hence gel will form only if $R_{min} = 1$. In this
limit also, like in the limit of $K_R \to 0$, as the value of β is
increased, R_{min} decreases and is to be expected as the blowing
agent behaves like a chain extending agent.

The effect of increasing K_R on R_{min} at constant β is
quite unexpected as R_{min} increases at first and decreases later.
This can be observed from figure 3. At low values of K_R, the
D group does consume A groups but at such slow rates that CD
monomer essentially behaves like a blocking agent. Hence,
increasing K_R from zero effectively leads to increased consumption
of A groups but not to effective chain extension as long as K_R
is sufficiently low. Thus initial increases in K_R from zero
will increase R_{min}. However as K_R is increased further the
blocking effect vanishes and CD will now participate in
effective chain extension or connecting branch points. This
effect will then decrease the requirements of A groups and hence
R_{min} will decrease. Another useful conclusion from these
results is that if K_R is increased to sufficiently high values
by catalysis, gels can still be obtained by addition of larger
amounts of blowing agent at constant R.

Figures 4 and 5 display the combined effects of K and
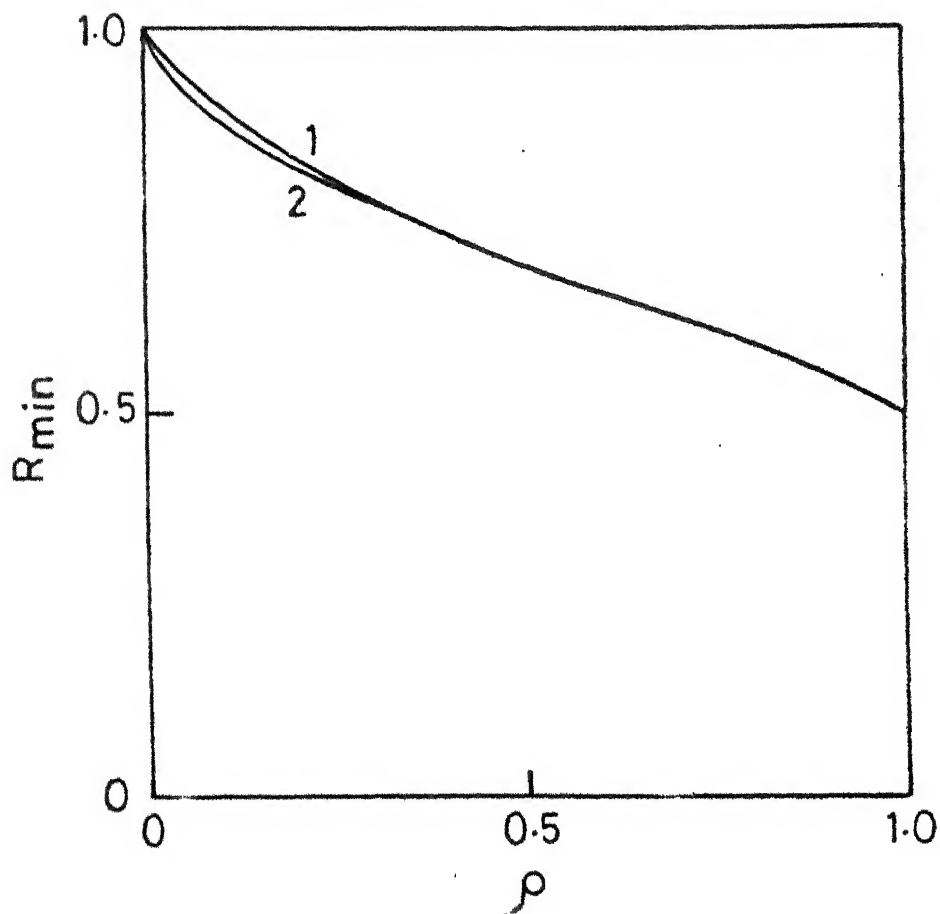K_R for different sets of values.

FIGURE 4 : Effect of K_R on R_{min}. K_R for the curves
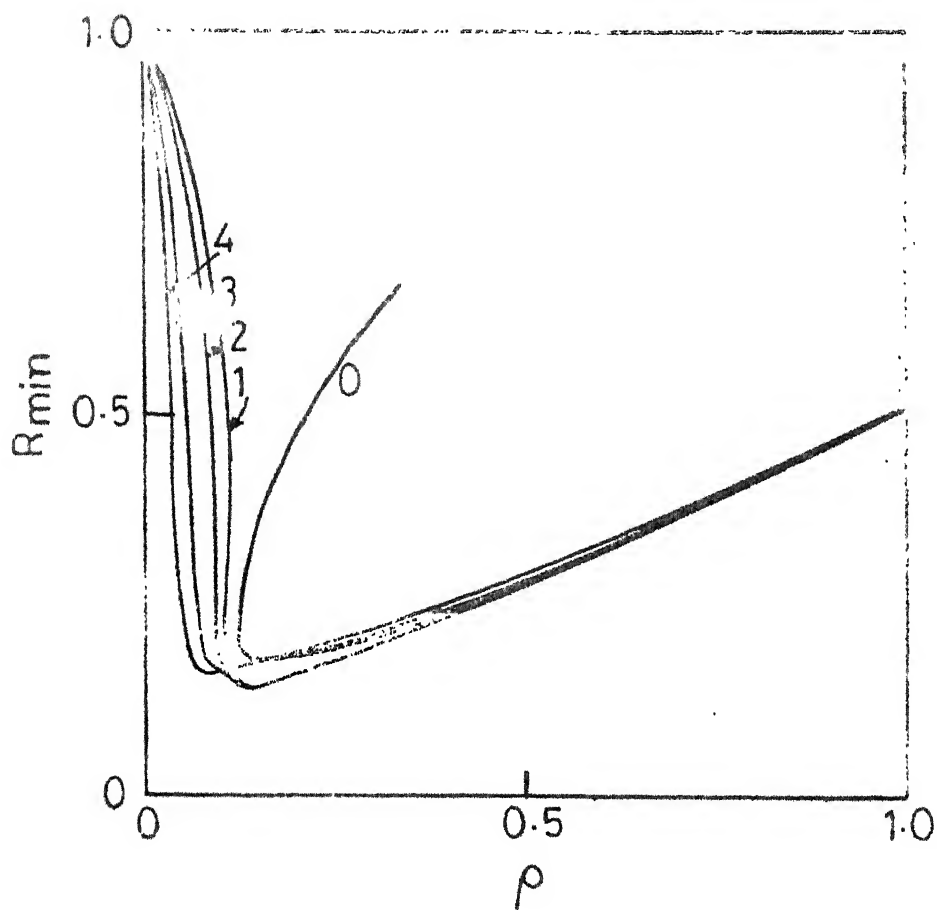1 and 2 are 0.1 and 5 respectively with
$K=5$

FIGURE 5 : Effect of K_R on R_{min}. Curves 0-4 are for K_R =0, 2, 2.5, 5 and 7.5 respectively with K = 0.1

(ii) R_{max} versus ρ : This gives the upper boundary of the gelation envelope. R_{max} will be greater than unity or the A groups are in stoichiometric excess and hence the upper boundary is obtained when $\rho = r = \xi = 1$. The only parameters of significance therefore are K_A, K_1 and K_2 as (35) and (36) now simplify to

$$\rho \;>\; \frac{1}{2} \quad \frac{1 + K_A}{\alpha^*_2 + K_A \alpha^*_1} - \frac{1}{2} \;\leqslant\; 1 \tag{45}$$

and

$$\frac{\alpha_1}{1 + K_A \alpha_1} \left[1 + \alpha^*_2 + K_A (1 + \alpha^*_1) \right] = \frac{2}{R} \tag{46}$$

In particular note that d does not have any effect. The only point common to all gelation envelopes is $\rho = 0$ and $R_{max} = 1$. This can be seen from (45) since if $\rho = 0$, (45) can be satisfied only if $\alpha^*_1 = \alpha^*_2 = 1$ which in turn implies that $\alpha_1 = \alpha_2 = 1$. Numerical results illustrating the effect of K_A, K_1 and K_2 are shown in figure 6.

Effect of K_A: Note that $K_A \geqslant 1$ since labelling of 1 and 2 on A groups is arbitrary. For simplicity let us first consider the case when $K_1 = K_2 = 1$. If the value of K_A is greater than unity, A_2 reacts faster than A_1 and hence if large amounts of A_1A_2 monomer are present, all B groups are consumed by A_2 groups leaving A_1 groups unreacted. To promote crosslinking the A_1 groups have to be forced to react and this can be achieved only by decreasing R at constant ρ . Thus the effect of increased value of K_A is to decrease R_{max}, as shown in figure 6 by curve 2.
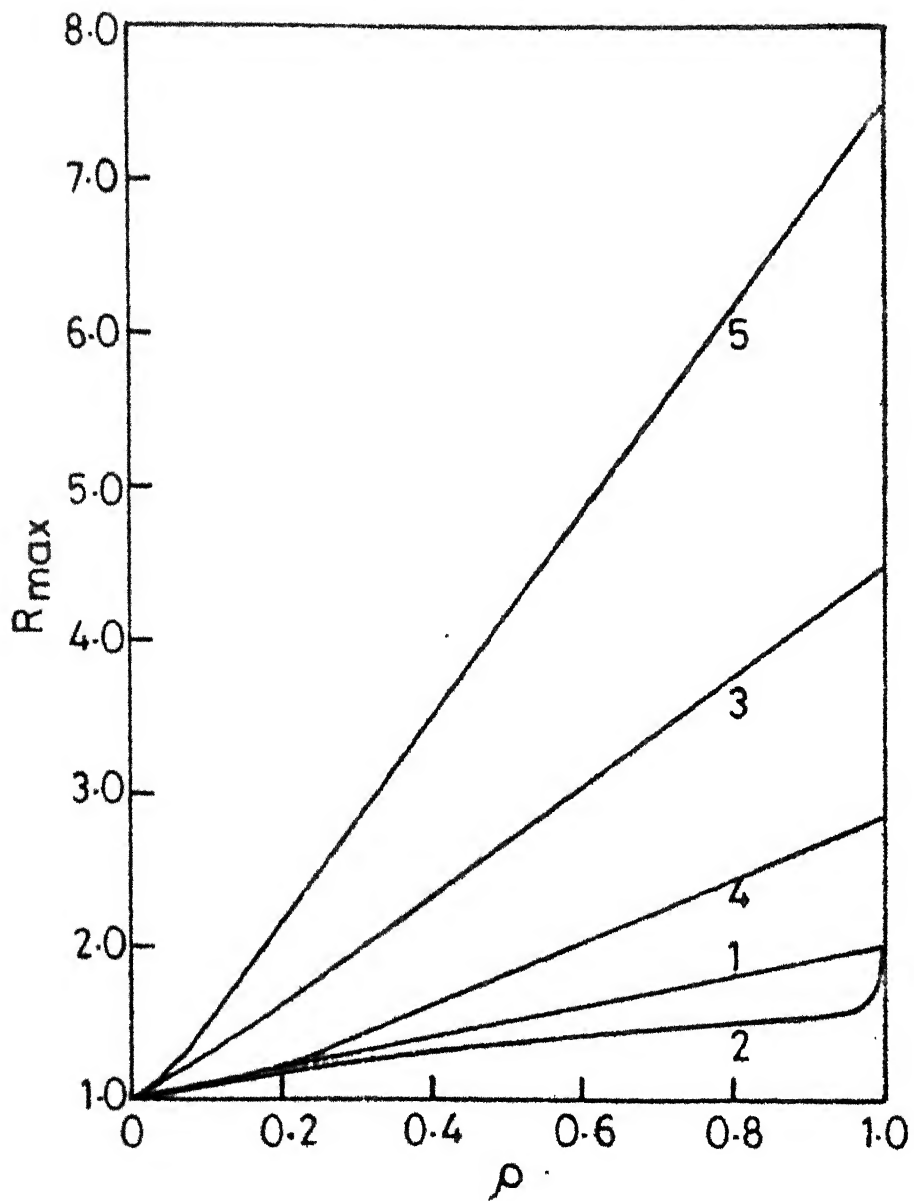
FIGURE 6 : Effect of K_A, K_1 and K_2 on R_{max}. The values of the above parameters for the various curves are: -1: 1,1,1,; 2:5,1,1,; 3:1, 4,4; 4:10, 10,10 and 5: 2.5, 10,10

Effect of K_1 or K_2: First consider the case when $K_* = 1$ and $K_1 = K_2$. If K_1 or K_2 is greater than unity the polymeric A groups react faster than monomeric A groups or the processes of connection of branch points and chain extension are promoted. Hence larger amounts of AA monomer can be utilised or R_{max} is increased at constant ρ. This is shown by curve 3 of figure 6.

At constant ρ therefore the effects of increased K_A and K_1 (or K_2) on R_{max} are in the opposite directions. The net effect is determined by the numerical magnitudes of these constants. This is illustrated in figure 4 by the other curves.

It is observed in all these curves that as ρ is increased R_{max} increases. When ρ is increased the fraction of B_f increases. Gelation will not occur if A_1A_2 monomer terminates all B,C,D groups without linking two branch points and this happens when A_1A_2 is in excess of R_{max}. However the chances of two branch points being connected are increased when the fraction of the polyfunctional groups or ρ is increased and therefore more A_1A_2 monomer can be tolerated by the reaction mixture. Hence as ρ is increased R_{max} also increases.

Gelation envelope in the presence of difunctional monomer:

The broad principles discussed in the previous sections will still hold in explaining the influence of the presence of B_2 monomer or when $d \neq 0$. Firstly it has already been noted that the R_{max} vs. ρ curve is not influenced by d and hence we need to discuss only R_{min} vs. ρ. The relevant parameters therefore are K and K_R only. The limiting results for K and $K_R \to 0$ and ∞ can easily be derived and will not be presented.

Moreover, the effects of K and K_R are unaltered by the presence of B_2 and hence need not be discussed. We shall focus our attention on the effects of d. It is convenient to recall that $\rho = (1-d)(1-b)$ by (28). Firstly it should be noted that the maximum permissible value for ρ is $(1-d)$ when $b = 0$. Further if d is increased while ρ is kept constant, it implies a decrease in the concentration of the blowing agent in the reaction mixture. The results therefore can be understood in terms of the relative effectiveness of B_2 and CD in creating connections between branch points. In the following discussion it is assumed that ρ is kept constant.

(i) $K = 0$: Here CD is a nonreactive diluent. Thus if d is increased, the fraction of B_2 monomer, which consumes A groups, is increased. We can therefore expect R_{min} to increase. This is shown in figure 7.

(ii) $K \rightarrow \infty$: Here CD is an instantaneously reacting blowing agent and hence consumes more A groups than B_2 monomer. Hence as d is increased, the slow reacting B_2 replaces the fast reacting CD resulting in a decreased R_{min}. This is shown in figure 8.

(iii) $K_R = 0$: The CD monomer is a monofunctional blocking agent which consumes A groups wastefully. Thus as d is increased we expect R_{min} to decrease as B_2 does not have any blocking effect. This is shown in figure 9.

(iv) $K_R \rightarrow \infty$: Here the CD monomer is more effective in chain extension and providing linkages than B_2 monomer, due to the fact that the D group reacts at a faster rate than a B group.
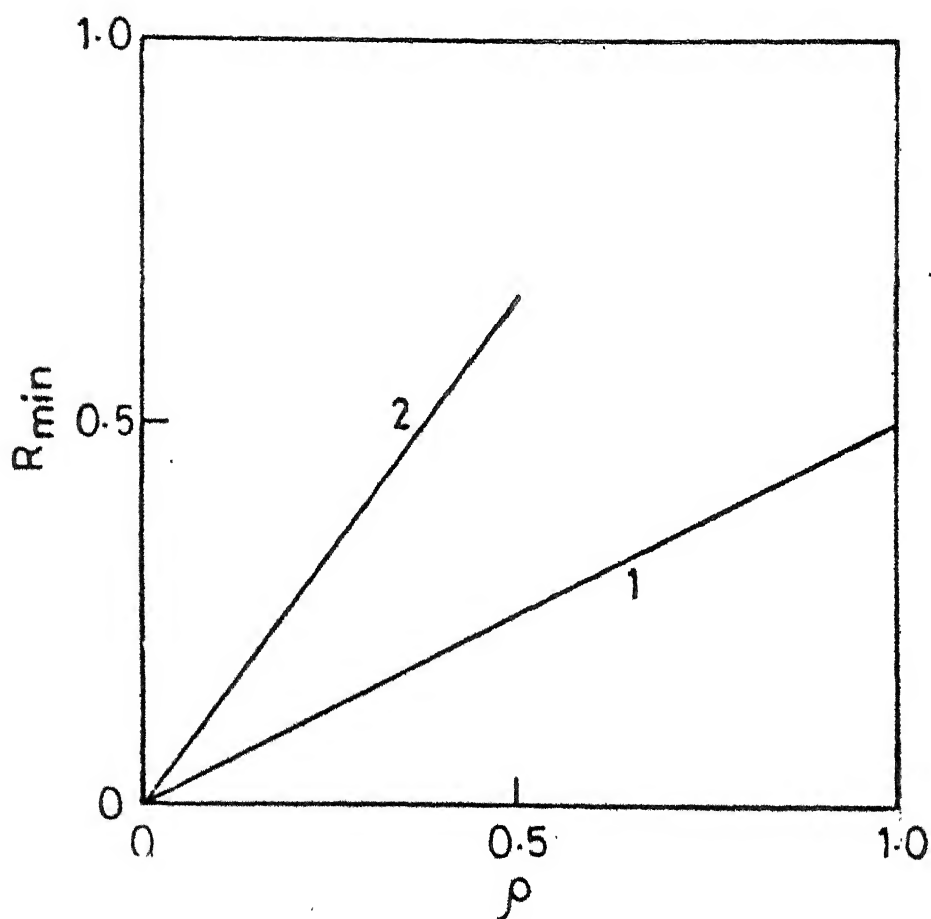
FIGURE 7 : Effect of the addition of the difunctional monomer on R_{max} for K=0. Lines 1 and 2 represent d = 0 and .5 respectively
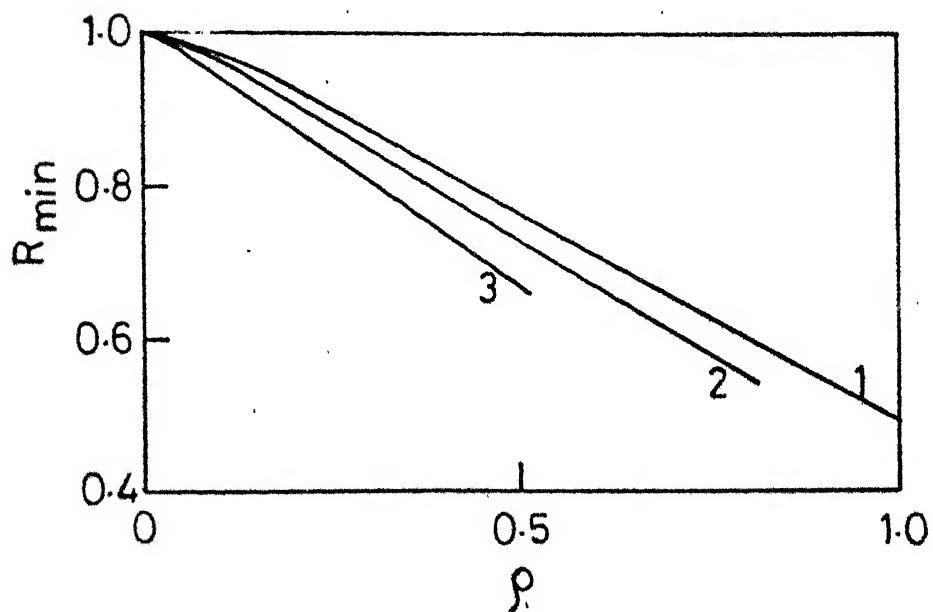
FIGURE 8 : Effect of addition of the difunctional monomer R_{min} for $K = \infty$. The curves 1-3 are for $d = 0$, 0.2 and 0.5 respectively
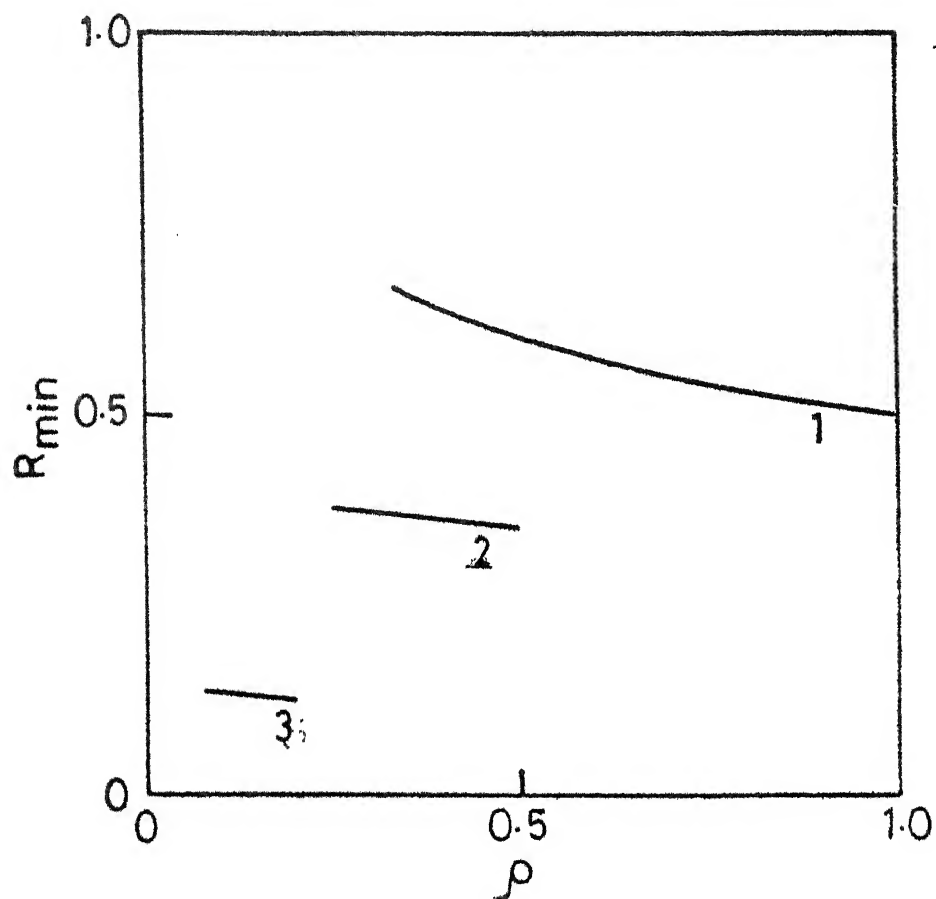
FIGURE 9 : Effect of addition of the difunctional monomer
on R_{min} for $K_R = 0$. The curves 1-3 for
for d = 0, 0.5 and 0.8 respectively.

Hence we can expect R_{min} to increase as d is increased. This is shown in Fig.10.

For values of K and K_R in between the above discussed limits, the behaviour is illustrated in figures 11 and 12 and can be explained along lines similar to the ones used above and in the previous sections.

Gel Point Calculation for Incomplete Conversions

The curves for incomplete conversions will lie inside the gelation envelope. If a value of α_1 (< 1) is fixed, all the other values of $\alpha_2, \alpha_1^*, \alpha_2^*, \xi, \gamma$ and ζ can be calculated from the kinetic parameters. For these probabilities, the values of R, and d that will satisfy (35) and (36) can be determined and plots of R versus γ can be generated. It was found that the effect of rate constants on such plots was similar to that observed on gelation envelopes. A typical plot is shown in figure 13. The curves start inside the lower half of the gelation envelope. To start with $\beta > 0.5$ and it steadily, increases as R is changed. At some value of R, β attains a value of unity. This particular value of R will lie on R_{max} vs. curve. Such parametric curves give an indication of the extents of conversion attained when gelation occurs for any initial composition specified by R, γ and d lying inside the gelation envelope.
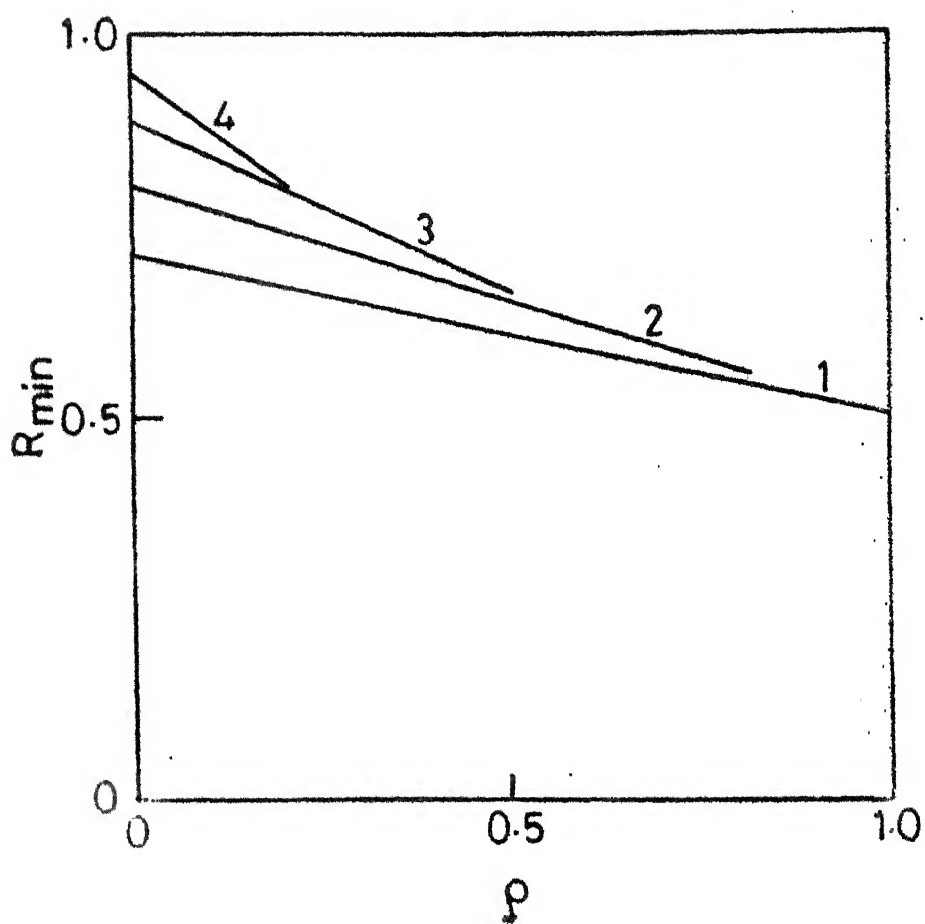
FIGURE 10 : Effect of addition of the difunctional
monomer on R_{min} for $K_R = \infty$. The curves
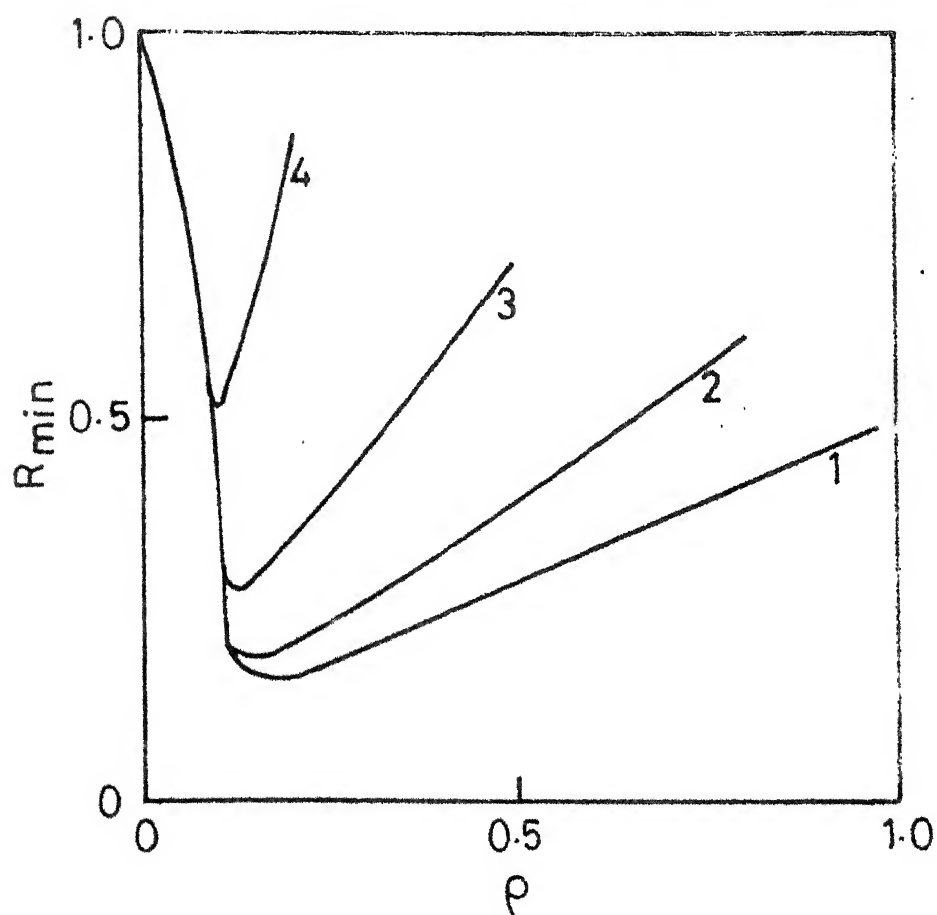1-4 are for d = 0, 0.2, 0.5 and 0.8
respectively.

FIGURE 11 : Effect of addition of the difunctional
monomer on R_{min} for $K = 0.1$ and $K_R = 1$.
The curves 1-4 are for $d = 0$, 0.2, 0.5
and 0.8 respectively.
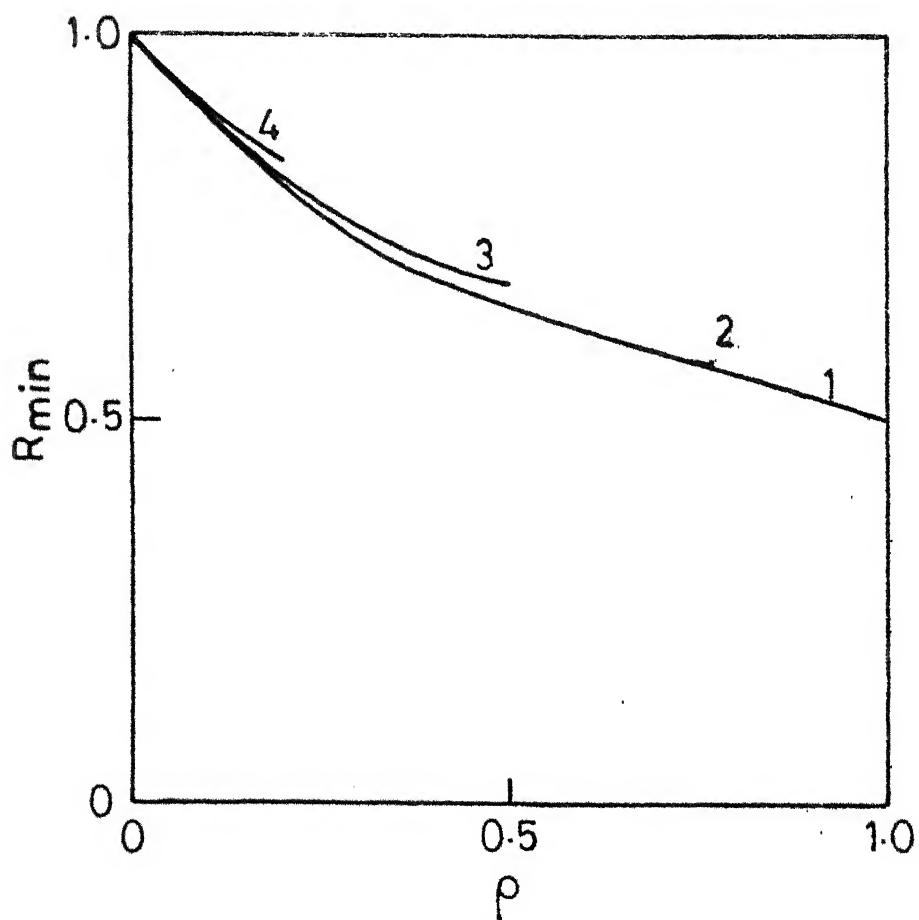
FIGURE 12 : Effect of difunctional monomer concentration
            on R_{min} for $K = 2$ and $K_R = 0.1$. Curves 1–4
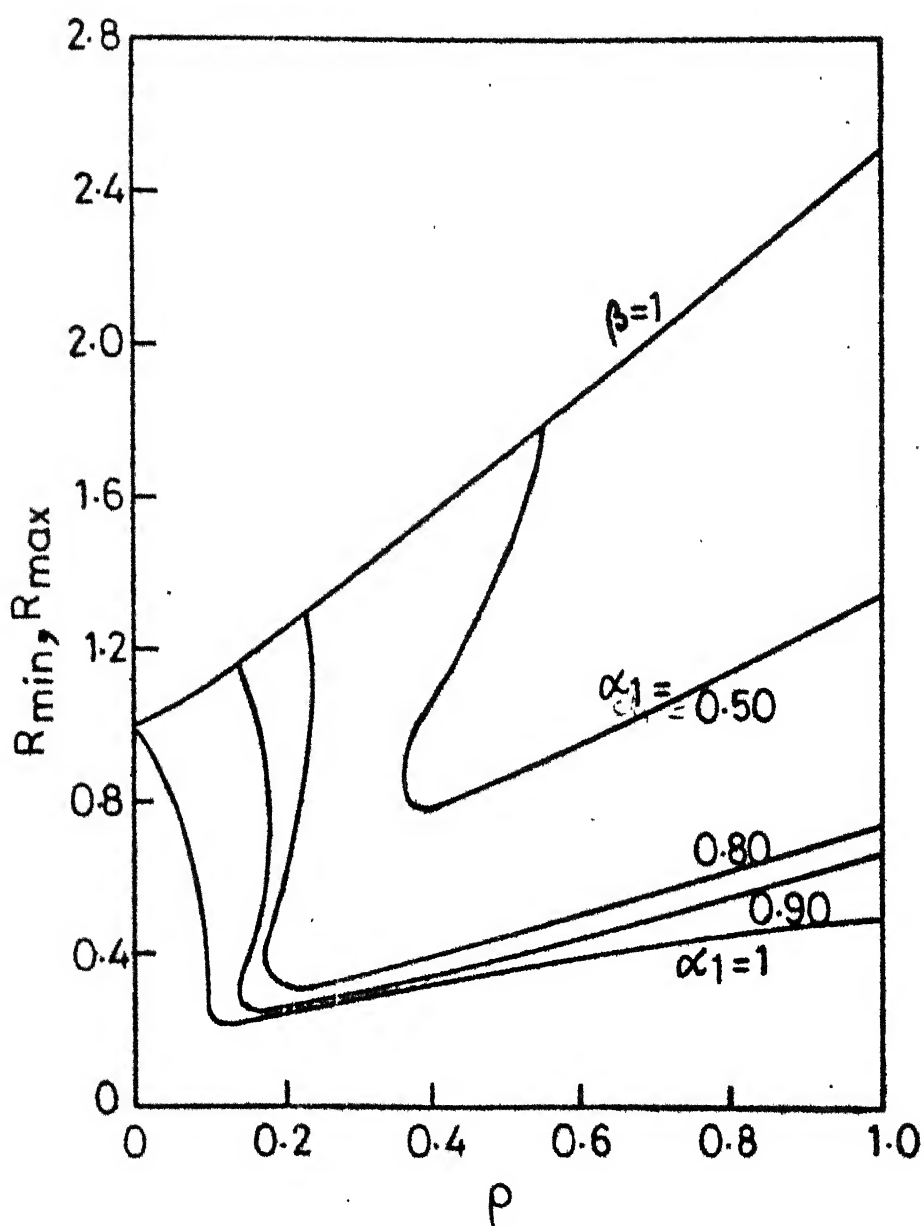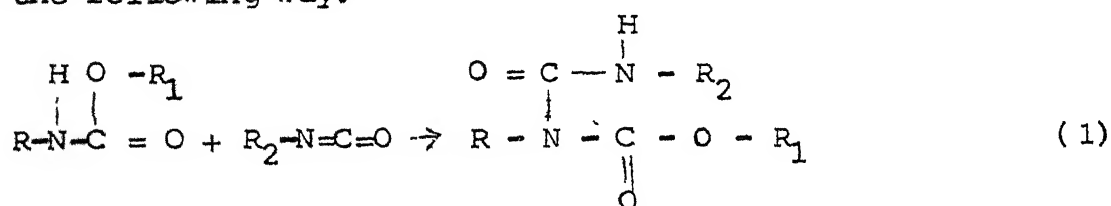   are for $d = 0$, 0.2, 0.5 and 0.8 respectively.

FIGURE 13 : Gelation envelopes for incomplete conversion
of all the monomers. The figure is for
$K = 0.1$, $K_R = 2$, $K_A = 2.0$, $K_1 = 1.5$ and
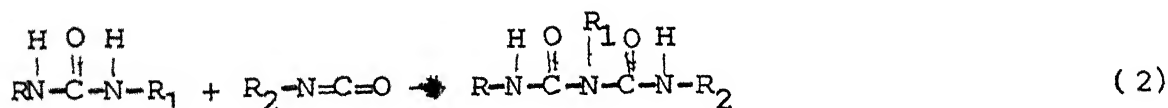$K_2 = 3.0$.

In the previous chapter the reactions of formation
of allophanate and biuret were assumed to be negligible.
But at higher temperatures these reactions are quite
competative[2,6]. Even otherwise it is necessary to look at the
effect of these reactions to determine whether their effect
on gelation is really negligible or not.

BASIC REACTIONS

Isocyanates can react with the free hydrogen of urethane
and urea linkage to give allophanates and biurets respectively
in the following way:

$$\begin{array}{ccc} & & H \\ & & | \\ H\ O\ -R_1 & O = C - N - R_2 \\ |\ | & | \\ R-N-C = O + R_2-N{=}C{=}O \rightarrow R - N - C - O - R_1 & \qquad (1) \\ & \| \\ & O \end{array}$$

urethane   isocyanate   Allophanate

$$\begin{array}{cc} H\ O\ H & H\ O\ R_1\ O\ H \\ |\ \|\ | & |\ \|\ |\ \|\ | \\ RN-C-N-R_1 + R_2-N{=}C{=}O \rightarrow R-N-C-N-C-N-R_2 & \qquad (2) \end{array}$$

urea   isocyanate   biuret

It can be seen from the above equations that the allophanate
reaction still leaves a free hydrogen for possible further
reaction. But this kind of reactions do not take place in the
industrial samples checked[2]. It is possible that the reaction
stops at this stage due to steric hindrance. This also
eliminates the possibility of the free hydrogen of biuret
reacting further since these hydrogens are similar to the
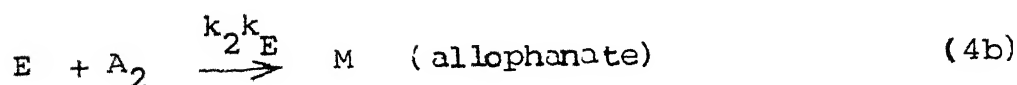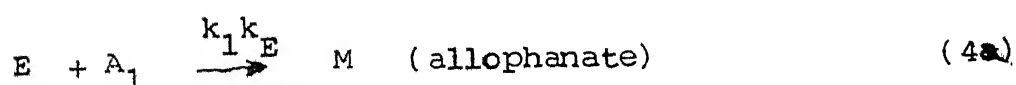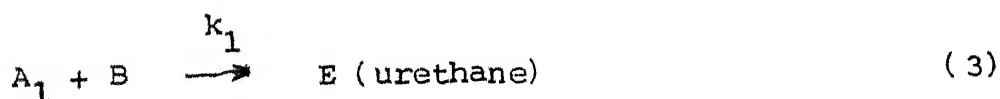hydrogens of the allophanate group.

MODEL OF THE SYSTEM

A system consisting only of a diisocyanate (A_1A_2), a polyol (B_f) and water (CD) is considered. The kinetics of each reaction is described below.

Reaction of isocyanate with polyol and water has already been described in Chapter 2 and the same is adopted here. The symbols for kinetic constants are also the same.

Allophanate:

Allophanate link is produced by the reaction of urethane with isocyanate. It is assumed that the rate of reaction differs from that with -OH by a proportionality constant K_x. A sample reaction step is as follows:

$$A_1 + B \xrightarrow{k_1} E \text{ (urethane)} \tag{3}$$

$$E + A_1 \xrightarrow{k_1 k_E} M \quad \text{(allophanate)} \tag{4a}$$

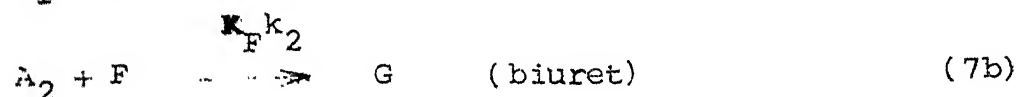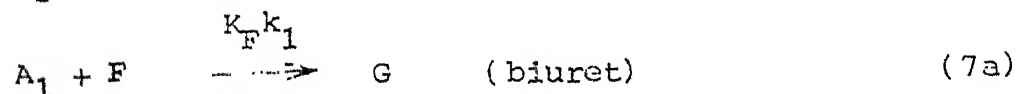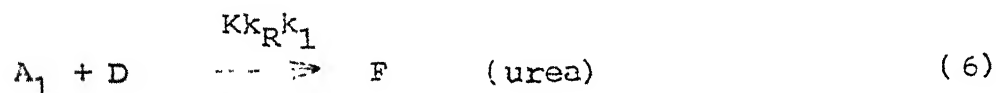$$E + A_2 \xrightarrow{k_2 k_E} M \quad \text{(allophanate)} \tag{4b}$$

Let ϵ be the fractional conversion to allophanate. It is defined to be the ratio of Allophanates formed to the total Allophanates that can be formed if all the B's reacted

Or,

$$\epsilon = \frac{(E)_0 - (E)}{(B)_0} \tag{5}$$

Biuret

The biuret reaction rate constant is assumed to differ from the urethane reaction rate constants by a proportionality constant of K_F and the reaction scheme is as follows:

$$A_1 + D \xrightarrow{\quad Kk_Rk_1 \quad} F \quad \text{(urea)} \tag{6}$$

$$A_1 + F \xrightarrow{\quad K_Fk_1 \quad} G \quad \text{(biuret)} \tag{7a}$$

$$A_2 + F \xrightarrow{\quad K_Fk_2 \quad} G \quad \text{(biuret)} \tag{7b}$$

Let $\emptyset$ be the fractional conversion to Biuret. It is defined to be the ratio of Biurets formed to the total that can be formed if all the C's reacted.

By writing the kinetic equations as before and solving them we can relate $\alpha_1^*, \alpha_2^*, \alpha_2, \gamma, \delta, \emptyset$ and $\in$ to α_1 and β with reaction constants as parameters (See Appendix B).

Stoichiometry

According to the above reaction scheme:

A's reacted = B's reacted + C's reacted + D's reacted + E's reacted + F's reacte

$$\text{L.H.S.} = A_0 \frac{\alpha_1}{1 + K_A\alpha_1} \left[1 + \alpha_2^* + K_A^*(1 + \alpha_1^*) \right] \tag{8}$$

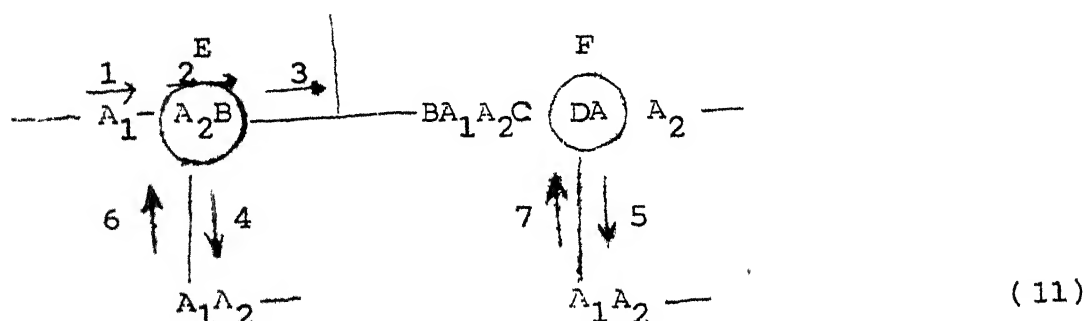$$\text{R.H.S.} = B_0\beta + C_0\gamma + C_0\delta + B_0\in + C_0\emptyset \tag{9}$$

Hence we obtain

$$R\frac{\alpha_1}{(1+K_A\alpha_1)}\left[1+\alpha_2^*+K_A(1+\alpha_1^*)\right]=2\rho(\beta+\epsilon)+(1-\rho)(\gamma+\delta+\phi)\tag{10}$$

GELATION CRITERION

Macosko's[5] approach is used below to determine the average molecular weight of the polyurethane. This leads to the gelation criterion after finding the condition for infinite molecular weight.

$$\tag{11}$$

As can be seen above, B, E and F can lead to a branch.

$$E(W_{A_2^*}^{out})=P(A_2\text{reacts})\left[P(B)\ P(E_{\text{Not react}})E(W_B^{in})\right.$$

$$+P(C)\ E(W_C^{in})+P(D)\ (F_{\text{Not react}})E(W_D^{in})$$

$$+P(B)P(E_{\text{reacts}})\left\{E(W_B^{in})+E(W_E^{out})\right\}$$

$$+P(D)P(F_{\text{reacts}})\left\{E(W_D^{in})+E(W_F^{out})\right\}$$

$$\left.+P(E)\ E(W_E^{in})+P(F)\ E(W_F^{in})\right]$$

$$+P(A_2\text{ not react})\ (0)$$

$$= P(A_2 \text{ reacts})\Big[P(B)E(W_B^{in}) + P(C)E(W_C^{in}) + P(D)E(W_D^{in})$$

$$+P(B)\ P(E_{reacts})E(W_E^{out}) + P(D)\ P(F_{reacts})\ E(W_F^{out})$$

$$+P(E)\quad E(W_E^{in}) + P(F)\ E(W_F^{in}) \Big] \tag{12}$$

Total B equivalent reacted $= B_o\beta + C_o(\gamma+\delta) + B_o\epsilon + C_o\phi$

$$B_E = B_o(\beta+\epsilon) + C_o(\gamma + \delta + \phi)$$

$$=(B_o + 2C_o)\Big[\rho(\beta+\epsilon) + \frac{(1-\rho)}{2}(\gamma+\delta+ \phi) \tag{13}$$

$$P(B)\quad = \rho\beta /\ B_E \tag{14}$$

$$P(C)\quad = \frac{(1-\rho)}{2}\ \gamma\ /\ B_E \text{ etc.} \tag{15}$$

$$E(W_B^{in}) = M_B + (f-1)\ E(W_B^{out}) \tag{16}$$

$$E(W_C^{in}) = M_C - M_{CO_2} + E\ (W_D^{out}) \tag{17}$$

$$E(W_D^{in}) = M_C - M_{CO_2} + E\ (W_C^{out}) \tag{18}$$

$$E(W_B^{out}) = P(B_{reacts})\Big[P(A_1)E(W_{A_1}^{in}) + P(A_2)E(W_{A_2}^{in})$$

$$+P(A_1)E(W_{A_1}^{in}) + P(A_2)E(W_{A_2}^{in}) \Big]$$

$$\tag{19}$$

$$E(W_E^{out}) = P\ (E_{reacts})\Big[\quad\quad -do- \quad\quad \Big] \tag{20}$$

$$E(W_E^{out}) = P\ (F_{reacts})\Big[\quad\quad -do- \quad\quad \Big] \tag{21}$$

$$P(E_{reacts}) = \epsilon/\beta \tag{22}$$

$$P(F_{reacts}) = \phi/\delta \tag{23}$$

All A's reacted = A_1 reacted + A_2 reacted + A_1^* reacted

$$+ A_2^* \text{ reacted}$$

$$= A_o \frac{\alpha_1}{(1+K_A\alpha_1)} \cdot (1+K_A) + A_o \frac{\alpha_1}{(1+K_A\alpha_1)} \cdot (\alpha_2^* + K_A\alpha_1^*)$$

$$= A_o \frac{\alpha_1}{(1 + K_A\alpha_1)} \cdot \left[1 + \alpha_2^* + K_A(1 + \alpha_1^*) \right] \tag{24}$$

$$P(A_1) = \frac{1}{1 + \alpha_2^* + K_A(1 + \alpha_1^*)} \tag{25}$$

$$P(A_2^*) = \frac{K_A\alpha_1^*}{1 + \alpha_2^* + K_A(1 + \alpha_1^*)} \quad \text{etc.} \tag{26}$$

$$E(W_B^{out}) = \frac{\beta}{1+\alpha_2^* +K_A(1+\alpha_1^*)} \left[E(W_{A_1}^{in}) + K_A\alpha_1^* E(W_{A_1^*}^{in}) + K_A E(W_{A_2}^{in}) \right.$$

$$\left. + \alpha_2^* E(W_{A_2^*}^{in}) \right]$$

$$= \beta x \tag{27}$$

$$E(W_C^{out}) = \gamma x \tag{28}$$

$$E(W_D^{out}) = \frac{\delta}{\gamma} x \tag{29}$$

$$E(W_E^{out}) = \frac{\epsilon}{\beta} x \tag{30}$$

$$E(W_F^{out}) = \frac{\phi}{\delta} x \tag{31}$$

$$E(W_E^{in}) = E(W_B^{in}) + E(W_A) \tag{32}$$

$$E(W_F^{in}) = E(W_D^{in}) + E(W_A) \tag{33}$$

$$E(W_A^{in}) = P(A_1) E(W_{A_1}^{in}) + P(A_2) E(W_{A_2}^{in}) + \ldots \tag{34}$$

$$= X$$

Now using the above equations in 12, we obtain

$$E(y^{out}_{\alpha^*_2}) = \frac{\alpha^*_2}{\rho(\beta+\epsilon)+(\frac{1-\rho}{2})(\gamma+\delta+\emptyset)}\left[\rho\beta\, M_B+(f-1)\beta\, X\,\rho\beta\right.$$

$$+\frac{(1-\rho)}{2}\gamma\left\{(M_C-M_{CO_2})+\frac{\delta}{\gamma}X\right\}+\frac{(1-\rho)}{2}\delta\left\{(M_C-M_{CO_2})+X\right\}$$

$$+\rho\epsilon\, X+\frac{(1-\rho)}{2}\,\emptyset\, X+\rho\epsilon\left\{M_B+(f-1)\beta\, X\right\}$$

$$+\frac{(1-\rho)}{2}\emptyset\left\{(M_C-M_{CO_2})+\gamma X+X\right\}\right]$$

$$=\alpha^*_2\left[A+BX\right] \qquad\qquad (35a)$$

where

$$A=\frac{\rho M_B(\beta+\epsilon)+\frac{(1-\rho)}{2}(M_C-M_{CO_2})(\gamma+\delta+\emptyset)}{\rho(\beta+\epsilon)+\frac{(1-\rho)}{2}(\gamma+\delta+\emptyset)} \qquad\qquad (35b)$$

$$B=\frac{(f-1)\rho\beta(\beta+\epsilon)+\frac{(1-\rho)}{2}(2\emptyset+2\delta+\emptyset\gamma)+2\rho\epsilon}{\rho(\beta+\epsilon)+\frac{(1-\rho)}{2}(\gamma+\delta+\emptyset)} \qquad\qquad (35c)$$

Substituting equation 35 in 27 we get:

$$\beta X=\frac{\beta}{1+\alpha^*_2+K_A\alpha^*_1}\left[M_A+\alpha^*_2(A+BX)+K_A\alpha^*_1(M_A+A+BX)\right.$$

$$\left.+K_A\left\{M_A+\alpha^*_1(A+BX)\right\}+\alpha^*_2(M_A+A+BX)\right]$$

$$=M_A+\frac{2A(\alpha^*_2+K_A\alpha^*_1)}{1+\alpha^*_2+K_A(1+\alpha^*_1)}+2BX\frac{(\alpha^*_2+K_A\alpha^*_1)}{1+\alpha^*_2+K_A(1+\alpha^*_1)}$$

or,

$$X = \frac{M_A + \dfrac{2A(\alpha_2^* + K_A\alpha_1^*)}{1 + \alpha_2^* + K_A(1 + \alpha_1^*)}}{1 - \dfrac{2B(\alpha_2^* + K_A\alpha_1^*)}{1 + \alpha_2^* + K_A(1 + \alpha_1^*)}} \qquad (36)$$

Molecular weight will be infinite if X is infinite hence gel criterion is

$$\frac{2B(\alpha_2^* + K_A\alpha_1^*)}{1 + \alpha_2^* + K_A(1 + \alpha_1^*)} \geqslant 1 \qquad (37)$$

Check with Results of Chapter 1:

Without secondary reactions, $\epsilon = \emptyset = 0$

Hence,

$$B = \frac{(f-1)\rho\beta^2 + (\frac{1-\rho}{2})z\delta}{\rho\beta + \frac{(1-\beta)}{2}(\gamma + \delta)}$$

Hence gel criterion is:

$$\frac{2\left[(f-1)\rho\beta^2 + (1-\rho)\delta\right](\alpha_2^* + K_A\alpha_1^*)}{\left[\rho\beta + \frac{1-\rho}{2}(\gamma + \delta)\right]\left[1 + \alpha_2^* + K_A(1 + \alpha_1^*)\right]} \geqslant 1$$

or,

$$2(f-1)\rho\beta^2(\alpha_2^* + K_A\alpha_1^*) \geqslant (1 + \alpha_2^*) + K_A(1 + \alpha_1^*) - 2(1-\rho)(\alpha_2^* + K_A\alpha_1^*)$$
$$\left[\rho\beta + (\frac{1-\rho}{2})(\gamma + \delta)\right]$$

or,

$$\frac{4(f-1)\rho\beta^2(\alpha_2^* + K_A\alpha_1^*)}{2\{\rho\beta + \frac{(1-\rho)}{2}(\gamma + \delta)\}\{1 + \alpha_2^* + K_A(1 + \alpha_1^*)\} - 4(1-\rho)\delta(\alpha_2^* + K_A\alpha_1^*)}$$

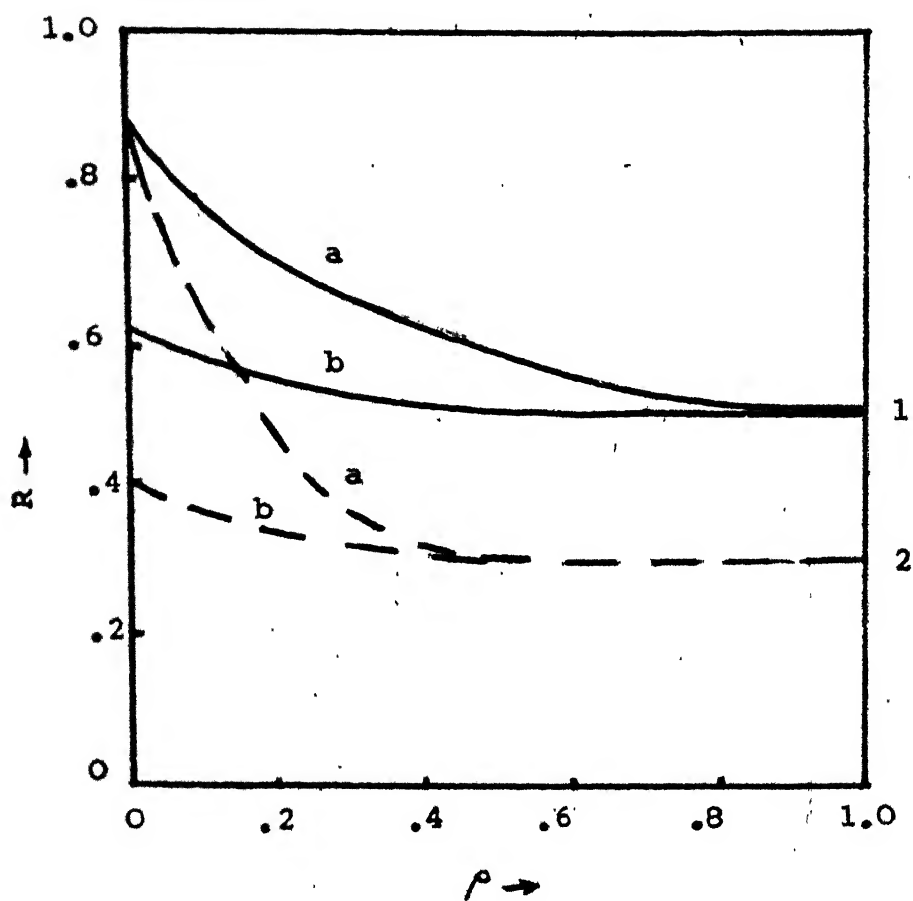which is same as before hence the results are consistent.

FIGURE 14 : Effect of Secondary Reactions on
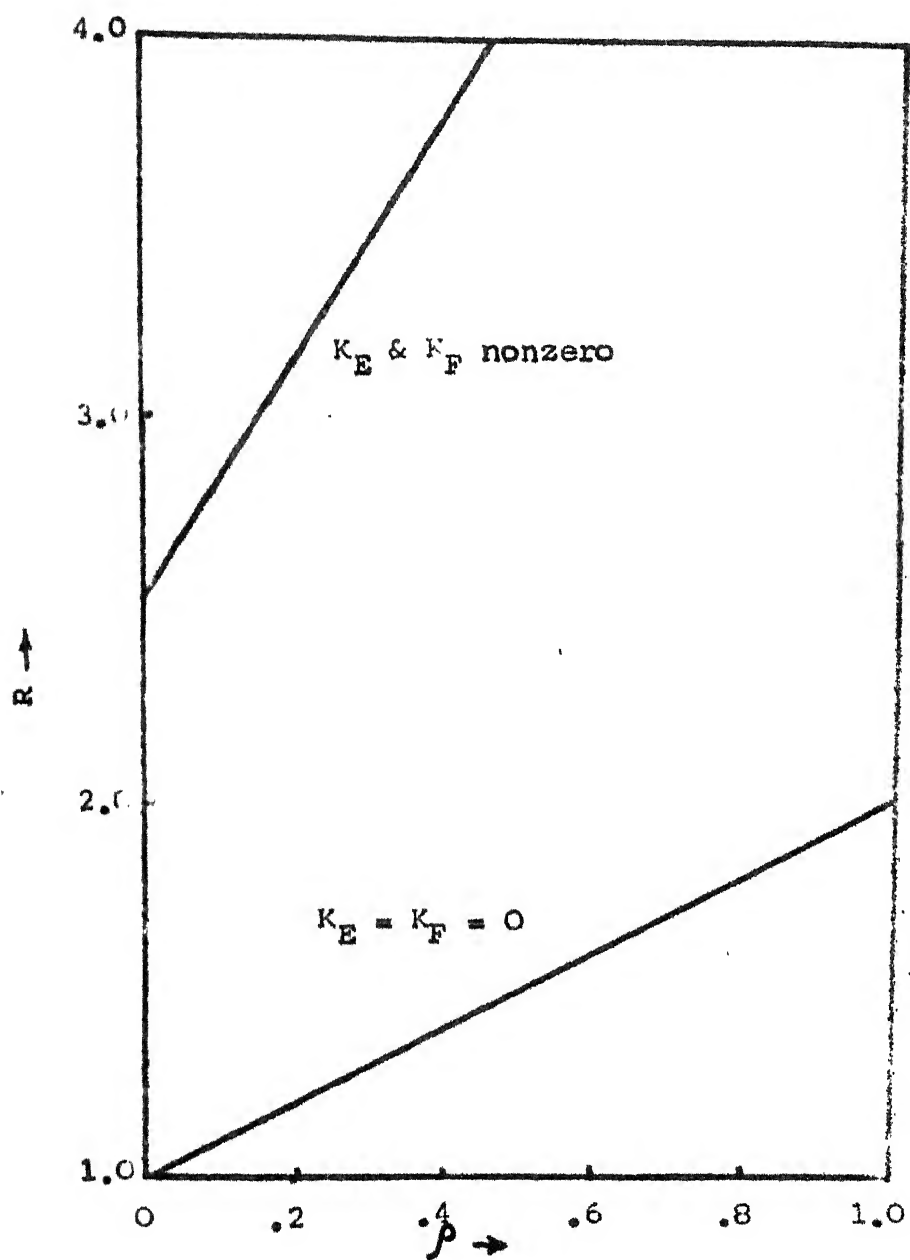R_{min}. $(K=1.0, K_R=1.0;$ $K_E=$ 1:.1,
3:1.0, K_F = 1: .1, b:5.0)

FIGURE 15: Effect of Secondary Reaction of
R_{max}.(K_A = 1.0, K_1 = 1.0, K_2=1.0)

RESULTS AND DISCUSSION

Using the expression obtained for the gelation criterion the gelation limits were calculated and they are presented in Fig.14 and 15.

R < 1

$\underline{\text{Effect of } K_E}$: As can be seen in Fig.14 the gelation limit R_{min} decreases as K_E is increased. This happens because as K_E is increased more Allophanate links are formed and the number of crosslinks increase, causing the gelation to occur at a lower conversion. Hence the gel limit decreases both for a given R as ρ_{min} decreases, and for a given ρ as R_{min} decreases.

$\underline{\text{Effect of } K_F}$: Increasing K_F has a similar effect as increasing K_E at low values of ρ. But at $\rho = 1$ since there are no urea linkages biurets are not formed and hence changing K_F has no effect. Also the effect of K_F is very small for small K and K_R values.

R > 1

As seen in Fig.15 for nonzero K_E and K_F values the R_{max} limit for gelation increased for a given ρ. This happens because, the Allophanate and biuret linkages consume A groups and make gelation possible even at a higher A group concentration. In absence of such linkages such an excess of A (Above the lower line in Fig.15) can block the polyfunctional B groups and make gelation infeasible.

Thus it is clear that the presence of secondary reactions lead to gelation of reactant mixtures which would not have been expected to gel. This is reasonable since these reactions (at $R < 1$) provide more crosslinks for the same number of B groups while (at $R > 1$) consuming more A's for the same number of B's. It has been shown how even with very small reaction rates these reactions can affect the limits considerably. Hence it is necessary that these reactions be taken into account while predicting the network properties.

It **is** known[17] that gel time measurement is a very good
method for determining the consistency and uniform quality of
the monomer batches used in industry. Consistency refers to
the constancy of the ratios of monomers fixed for the particular
system while uniform quality refers to the constancy of the
purity of the chemical constituents of the system. Geltime method
is applied to test these because geltime is sensitive to both
reactant ratio as well as the reaction rates.

Typical observed geltime curves[17] are shown in Fig.16.
The two curves were obtained for two different systems
as indicated in the figure. These figures show some interesting
characteristics. Firstly there is a minimum geltime which may
lie either above or below a NCO/OH of 1. The second property
of these curves is that they show a lower and an upper values
of NCO/OH where geltime is infinite. These ratios will be
referred to as **lower** and **upper** gel limits. Beyond these limits
gelling is not possible as **gela**tion occurs when deficient
reactant reacts completely. It is the purpose of this chapter to
show that these two characteristic properties are explained by
the models proposed in this work. The curves in Fig.16 were
obtained for solid elastomer systems where no foaming
agent was used.

MODEL FITTING

First an effort is made to use an equal reactivity
model for diisocyanates, diol and triol to fit this data. The
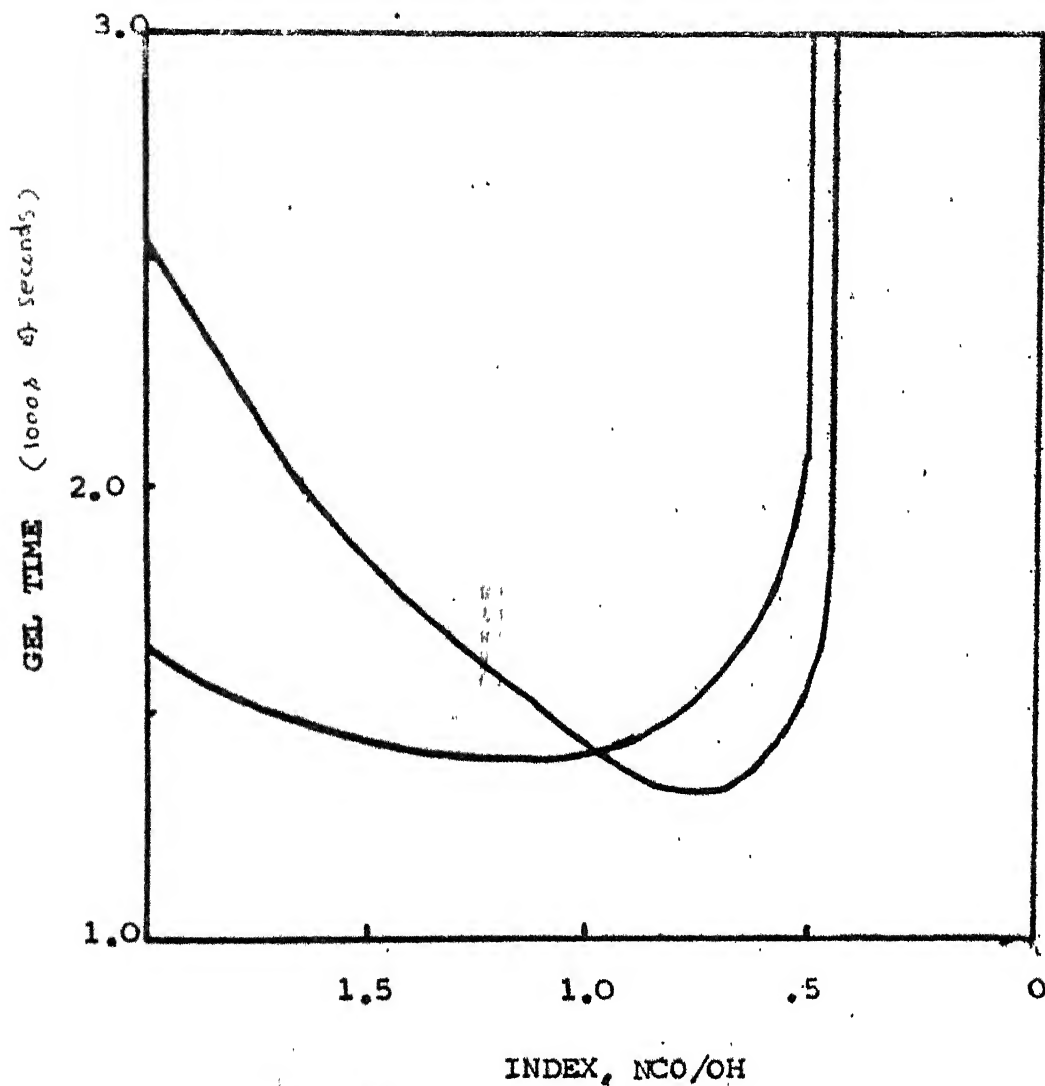geltime curve for the equal reactivity case (with $\phi = 1$, i.e.

FIGURE 16 : Experimental geltime curves (Ref.17).
Isocyanate used in PAPI®. The Polyols
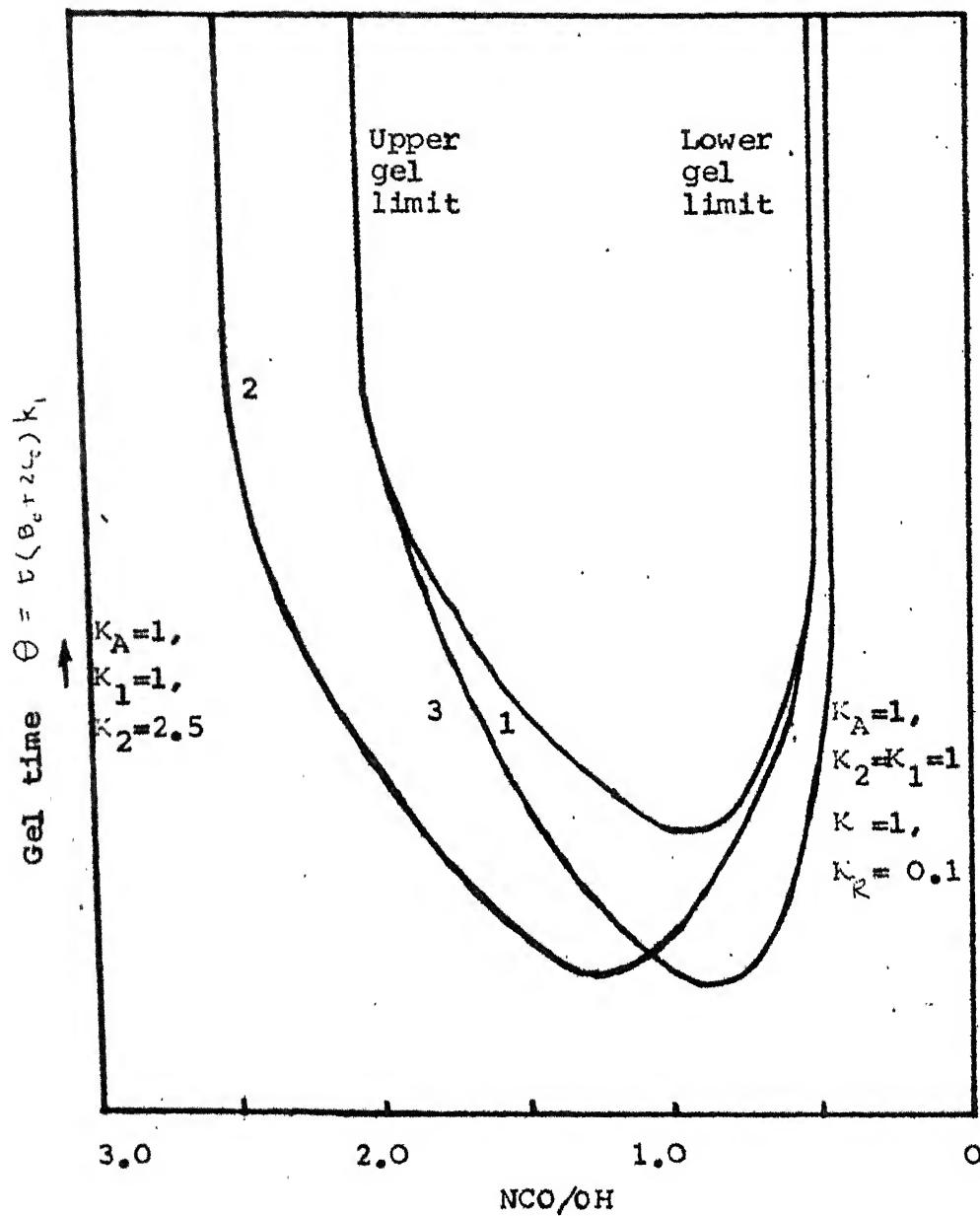used are Ethyl trimethylol propane and an
isonol.

FIGURE 17: Calculated geltime curves. 1: Equal
         reactivity case. 3: $K_A=1$, $K_1=1$, $K_2=1$,
    $K_E = 1.0$, $K_F = 0.1$, 2: $K_A=1$, $K_1=1$, $K_2=2.5$

ordinate not to scale.

no water) is shown in Fig.17 (curve 1). The curve has the same
overall shape as experimentally obtained curves of Fig.16.
But a   closer look reveals its limitations. While the
position of the lower geltime is alright the position of the
upper gel limit is at NCO/OH = 2 and the position of the minimum
is at NCO/OH = 1. Hence this model is inadequate for the
general system which may have a minimum at NCO/OH $\neq$ 1 and an
upper gel limit above 2.

   To overcome the short comings of the above model,
unequal reactivity of diisocyanate was introduced into
the model. The results obtained are depicted in curve 2 of
fig.17. This shows a minimum geltime at NCO/OH $>$ 1 and an
upper gel limit at NCO/OH $>$ 2. This can be explained by the
fact that infinite geltime indicates that at gel limits there is
complete conversion either of OH (R $>$ 1, upper gel limit) or
of NCO (R $<$ 1, lower gel limit) and as shown in Fig.17, for $\alpha_r = 1$
and at $\beta =$ 1 an upper gel limit of R $>$ 2 is possible in
unequal reactivity case. But this model failed to predict a
minimum in geltime at NCO/OH $<$ 1. Inclusion of various
possibilities (presence of moisture as an impurity or that
$\beta <$ 1, functional group of Polyol $\neq$ 3) did not alter this
prediction. It was therefore found necessary to incorporate
unequal reactivity of triols to explain this behaviour. Unequal
reactivity of triols alone did not predict an upper gel point at
NCO/OH $>$ 2 as shown by curve 3, Fig.17. Hence a model accounting
for unequal reactivities of hydroxyl and isocyanate groups is
required. The model is described below.

DESCRIPTION OF MODEL

The hydroxyl groups of diol are taken to be equally reactive since the molecule is generally large and symmetric. But the hydroxyl groups of the triol are assumed to have unequal reactivity of the structural asymmetry type. This triol can thus be represented as,

$$
\begin{array}{c}
B_2 \\
| \\
B_1 \rule{2cm}{0.4pt} B_1
\end{array}
\qquad (1)
$$

The reactivities of these B_1 and B_2 groups are assumed to differ from the B groups (diol) by proportionality constants K and K_R respectively.

Thus,

$$A_2 \; + \; B \; \xrightarrow{\;\;k_1\;\;} \; \text{product} \qquad (2a)$$

$$A_1 \; + \; B_1 \; \xrightarrow{\;\;K\,k_1\;\;} \; \text{product} \qquad (2b)$$

$$A_1 \; + \; B_2 \; \xrightarrow{\;\;K_R k_1\;\;} \; \text{product} \qquad (2c)$$
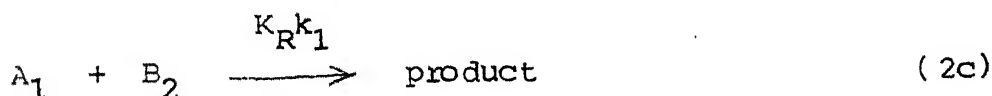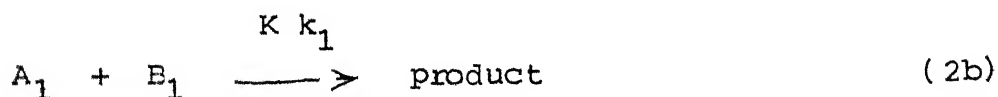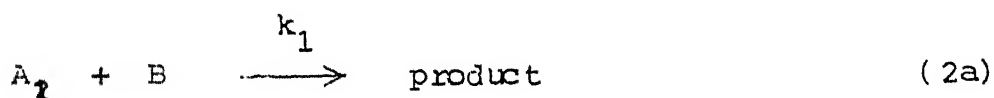
The method developed by Miller and Macosko[7] (also see Chapter 2) was used to derive the gel criterion. The following definitions were used:

$$B_{3_o} \; = \; \text{initial concentration of triol molecules} \qquad (3a)$$

$$[B_1]_o \; = \; \text{initial concentration of } B_1 \text{ groups} = 2B_{3_o} \qquad (3b)$$

$$[B_2]_o \; = \; \text{initial concentration of } B_2 \text{ groups} = B_{3_o} \qquad (3c)$$

B_{2_C} = initial concentration of diols (3d)

B_O = $2B_{2_O}$ = initial concentration of B groups (3e)

The concentration of A groups are represented as in Chapter 1

$$R = 2A_O / (2B_{2_O} + 3B_{3_O}) \tag{3f}$$

$$\beta = 3B_{3_O} / (2B_{2_O} + 3B_{3_O}) \tag{3g}$$

The fractional conversion of B, B_1 and B_2 are defined as:

$$\beta = (2B_{2_O} - [B]) / 2B_{2_O} \tag{4a}$$

$$\beta_1 = (2B_{3_O} - [B_1]) / 2B_{3_O} \tag{4b}$$

$$\beta_2 = (2B_{3_O} - [B_2]) / 2B_{3_O} \quad \bullet \tag{4c}$$

where $[B]$, $[B_1]$ and $[B_2]$ are the concentrations of B, B_1 and B_2 respectively in the solution.

Using the same approach as that used in Chapters 1 and 2, we obtain

$$(1 - \beta_1) = (1 - \beta)^K \tag{5a}$$

$$(1 - \beta_2) = (1 - \beta)^{K_R} \tag{5b}$$

and gel criterion is:

$$1 \leqslant 2\beta Y \frac{(\alpha_2^* + K_A \alpha_1^*)}{(1 + \alpha_2^* + K_A(1 + \alpha_1^*))} \tag{6}$$

where

$$Y = \frac{(1 - \beta) + \frac{2\beta}{3\beta}(\beta_1^2 + 2\beta_1 \beta_2)}{(1 - \beta)\beta + \frac{\beta}{3}(2\beta_1 + \beta_2)}$$

The definitions of conversions of isocyanate groups and their interrelations remain the same as in Chapter 2. The stoichiometric relation then is given by

$$\frac{R\alpha_1 \left\{ 1 + \alpha_2^* + K_A(1 + \alpha_1^*) \right\}}{2(1 + K_A\alpha_1)} = (1-\beta)\beta + \frac{\rho}{3}(2\beta_1 + \beta_2) \qquad (7)$$

Thus the conversions at gel point and in particular α_1 can be computed using the above formulae.

CALCULATION OF GELTIME

Geltime at a given NCO/OH ratio was calculated by solving the first order differential equation

$$- \frac{d[A]}{dt} = k_1(1 + K_A) [A] \left([B] + K[B_1] + K_R[B_2] \right) \qquad (8a)$$

which is the equation for consumption of diisocyanate monomer. This can be simplified in terms of the conversions as

$$\frac{d\alpha}{d\Theta} = -\alpha \left[(1-\beta)(1-\beta) + K(1 - \beta_1) \frac{2\rho}{3} + K_R(1 - \beta_2) \frac{\rho}{3} \right] \qquad (8b)$$

where,

Θ = dimensionless time

$= -k_1 t(3B_{3_0} + 2B_{2_0})$

This equation with equation 5, 7 and equations A13,14 and 15 from Appendix A was integrated by Runge-Kutta-Vernier method (IMSL subroutine) to a value of α_1 that satisfies the gel criterion 6. For a given set of reaction rate constant ratios, geltime was determined at various values of initial

NCO/OH ratios and the position of minimum in geltime was graphically located. An example each where geltime minimum occurs at NCO/OH $<$ 1 and $>$ 1 respectively is given below:

Case 1: Geltime below NCO/OH = 1

K_1 = 0.5, K_1 = 0.75, K_2 = 3.0, K = 1.0, K_R = 0.1,
= 0.2

NCO/OH	Geltime (dimensionless)
0.5	infinite
0.7	7.16
0.85	4.74
0.95	4.56
1.00	4.59
1.05	4.70
1.10	4.86

Clearly the minimum geltime lies below an NCO/OH of 1.0.

Case 2: Geltime above NCO/OH = 1

K_1 = .5, K_2 = .5, K_A = 1.0, = 1

NCO/OH	Geltime (dimensionless)
0.5	infinite
0.6	4.1
0.8	2.9
1.0	2.45
1.5	2.3
1.9	3.3
2.0	infinite

To illustrate the position of the gel limits the following example will suffice:

for $K_1 = 4.0$, $K_2 = 4.0$ and $K_A = 1.0$. The position of upper gel limit is at 4.5 as seen from Fig.6.

It is concluded that inclusion of unequal reactivities of OH as well as NCO isnnecessary and sufficient to enable the prediction of the two special characteristics of Fig.16, experimentally known for polyurethane elastomers.

In many polyurethane foam systems water is used as a blowing agent to produce CO_2 on reaction with NCO. At low molecular weight of the mixture the viscosity of Polyurethane is low and CO_2 bubbles evolved will escape. At very high molecular weight the polyurethane is elastic and CO_2 evolved may elastically stretch the matrix which may contract after cooling, resulting in a change in dimension of the product. Hence there is a molecular weight range between which the CO_2 evolved is effectively used. A discussion of this mechanism can be obtained elsewhere[6].

In this chapter the intention is to calculate the CO_2 evolved versus molecular weight. Such information is important because it points out how much CO_2 will be effectively trapped.

CALCULATION OF CO_2 EVOLUTION AND AVERAGE MOLECULAR WEIGHT

CO_2 is evolved according to equation 1.2 (Chapter 1, equation 2). The cumulative amount of CO_2 evolved can be found from the conversion of C and the rate from rate of consumption of C. The molecular weight can be calculated from the conversion of the functional groups using the approach of Macosco et al.[5] as shown below. For brevity the detailed steps are not reproduced here. The formula is given below:

$$\bar{M}_W = E(A)\ E(W_A) + E(B_f)\ E(W_{B_f}) + E(B_2)\ E(W_{B_2}) + E(C)\ E(W_C) \tag{1}$$

$$E(W_A) = M_A + \frac{(1 + K_A + \alpha_2^* + K_A \alpha_1^*)}{(1 + K_A \alpha_1)}(X + Y\ E(W_B^{out}))$$

$$E(W_{B_f}) = f\ E(W_B^{out}) + M_{B_f}$$

$$E(W_{B_2}) = 2\,E(W_B^{out}) + M_{B_2}$$

$$E(W_C) = (1-\gamma)\,M_C + \gamma\left[(M_C - M_{CO_2}) + (1+\frac{\delta}{\gamma})\,\frac{E(W_B^{out})}{\beta}\right]$$

$$E(A) = R/2\,L$$

$$L = R/2 + \rho/f + d/(1-d)\cdot\rho/2 + \frac{1-d-\rho}{2(1-d)}$$

$$E(B_f) = \rho/fL$$

$$E(B_2) = \frac{d}{(1-d)}\,\frac{\rho}{2L}$$

$$E(C) = \frac{1}{2}\,(\frac{1-d-\rho}{1-d})/L$$

$$E(W_B^{out}) = \frac{BM_A + 2\beta X\,\dfrac{(\alpha_2^* + K_A\alpha_1^*)}{(1 + K_A + \alpha_2^* + K_A\alpha_1^*)}}{1 - 2\beta Y\,\dfrac{(\alpha_2^* + K_A\alpha_1^*)}{(1 + K_A + \alpha_2^* + K_A\alpha_1^*)}}$$

$$X = \frac{\rho\beta\left[M_{B_f} - d(M_{B_f}-M_{B_2}) + (M_C - M_{CO_2})(\frac{1-d-\rho}{2})(\gamma+\delta)\right]}{\rho\beta + \frac{(1-d-\rho)}{2}(\gamma+\delta)}$$

$$Y = \frac{\rho\beta\left[(1-d)(f-1) + d\right] + \frac{(1-d-\rho)}{2}(\frac{2\delta}{\beta})}{\rho\beta + \frac{(1-d-\rho)}{2}(\gamma+\delta)}$$

$\alpha_1^*, \alpha_2^*, \gamma, \delta$ etc. are calculated by the equations derived in Appendix A.

$\alpha = (1-\alpha_1)/(1 + K_A\alpha_1)$ is calculated from the following kinetic expression derived from the conservation equation of AA monomer (Equation A1 of Appendix A).

$$\frac{d\alpha}{d\theta} = \frac{(1 + K_A)}{(1 - \alpha)} \alpha \left[\rho(1-\beta) + \frac{K(1-d-\int^\rho)}{2} \left\{ (1-\gamma) + K_R(\gamma-\delta) \right\} \right] \tag{2}$$

where,

$$\theta = t\, k_1\, (B_0 + 2C_0) = \text{dimensionless time}$$

is calculated from stoichiometric equation 1.36.

Equation 2 was solved with Runge-Kutta method to obtain conversions at different times and molecular weights as well as CO_2 evolved.

DISCUSSION

In Fig.18 the CO_2 evolution rate is plotted against log $(\bar{M}_w)$ for constant ρ with R as parameter. From the figure it can be seen that as R increases the CO_2 evolved for a given $\bar{M}_w$ increases. This can be easily explained. A higher value of R implies a higher number of NCO groups per OH groups and hence to achieve a given $\bar{M}_w$, i.e. same average number of branch points per molecular, a higher conversion of OH groups is required. This also implies that a higher number of water molecules have reacted leading to evolution of larger amount of CO_2.

In Fig.19 R is constant while ρ is the parameter for CO_2 evolution vs. log $(\bar{M}_w)$ curve. It is observed that as ρ increases CO_2 evolved for a given $\bar{M}_w$ decreases. This happens because to achieve a given $\bar{M}_w$ a system with higher ρ requires a lower conversion. At the same time the amount of water available is low. Both these factors lead to a lower CO_2 evolution for higher ρ value.
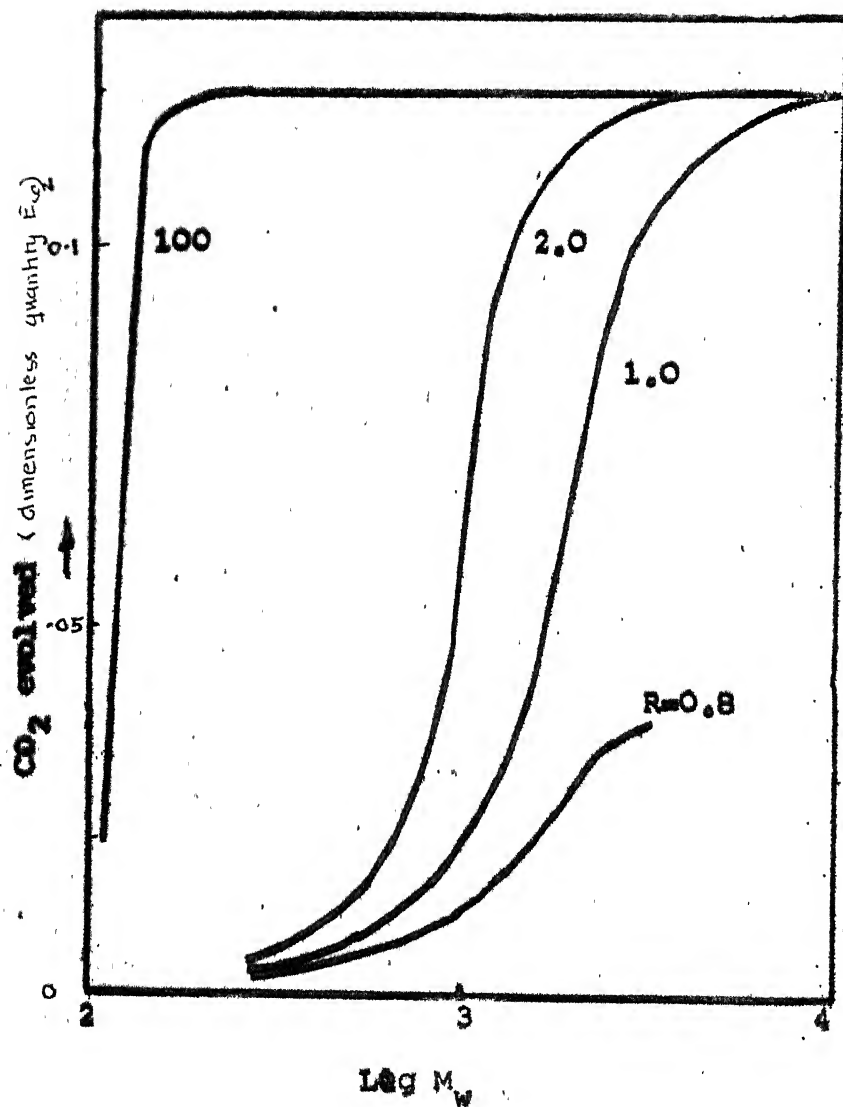
FIGURE 18: CO_2 evolved versus $\log (\bar{M}_W)$, R
as parameter. ($\rho = 0.5$, K = 0.1).

$E_c = (1-\rho)\Upsilon/2$
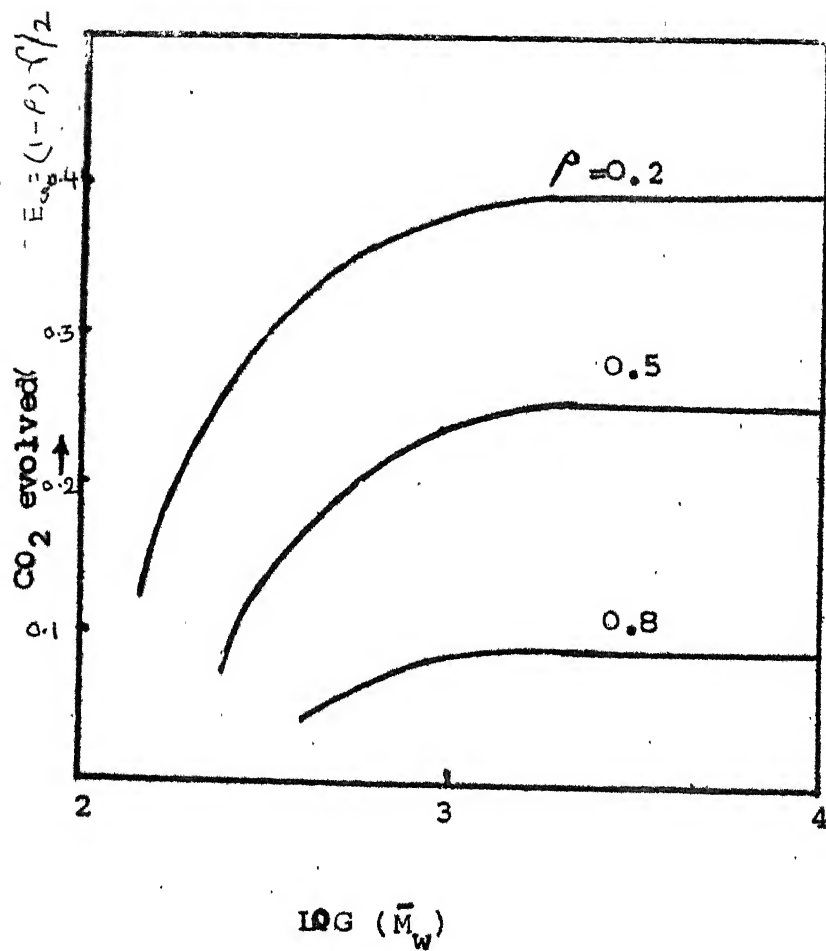
FIGURE 19: CO_2 evolved versus log $(\bar{M}_W)$,
ρ as parameter. ($R=1.0, K=5.0$).

$$E_{CO_2} = (1-\rho)\, \Upsilon/2$$

USES

Once such plots have been obtained they can be used to design the system. For example in Fig.18 if $\bar{M}_w = 1000$ is the most desirable molecular weight at which CO_2 should evolve then $R = 2.0$ is the best value to use whereas $R = 1.0$ or 100 is unsatisfactory. To be able to use $R = 1.0$ we have to change the reactivity ratios in the appropriate direction using catalysts.

CONCLUSIONS

In Chapter 2 a model for describing the curing behaviour of a monomer with unequal reactivity effects has been developed and applied to systems consisting of a diisocyanate ($A_1 A_2$), a polyol (B_f), a diol (B_2) and foaming agent water (CD). The gelation condition was derived and it predicts (i) whether a given initial composition of the reaction mixture will lead to a gel or not and (ii) the fractional conversions of functional groups required before gelation can occur.

Gel formation at complete conversion of the groups in stoichiometric deficiency defines the boundaries of gelation envelope and only those initial compositions which lie inside the envelope can lead to the formation of infinite networks. The boundaries of the gelation envelope have been presented as a plot of the ratio of the concentration of A groups and the concentrations of groups with which A can react, R_{max} or R_{min}, versus the fraction of the polyfunctional groups ρ.

Water can influence gelation behaviour in three ways by acting like a non-reactive diluent, a monofunctional blocking agent and an effective chain extender linking branch points. As the water content in the reaction mixture is decreased, R_{min} would increase if it were to operate like a nonreactive diluent and R_{min} would decrease if the other two ways were operative. The total behaviour is a combination of all the three aspects and is determined by the relative speeds of reaction of water and hydroxyl groups.

The asymmetric characteristics of the $A_1 A_2$ monomer can either promote or retard chain extension. Structural asymmetry retards chain extension. A first shell substitution effect that makes polymeric A ends to react faster than monomeric A ends promotes chain extension. At a constant P, R_{max} was found to increase if the overall effect of structural asymmetry and first shell substitution effect was to promote chain extension.

Calculation of conversions at which infinite networks form for compositions which lie inside the gelation envelope has also been illustrated.

The calculations show (see Fig.6) that an unequally reactive system may gel when an equal reactivity model predicts that gelation will not occur (curve 4 for example) it may also not gel when equal reactivity model predicts that gelation is possible (curve 2). Hence it is important to consider unequal reactivity while making such predictions.

The effect of secondary reactions has been shown to be not negligible (See Fig.14 and 15) for $R > 1$, presence of secondary reactions increases the limit R_{max} for gelation. This means that while a model which does not consider secondary reaction may predict that system will not gel, in reality it may gel. For $R < 1$, secondary reactions lower the limiting R_{min}. This means that the system which might be predicted to not gel may gel. Hence it is necessary to include secondary reactions in the model for correct prediction of gel limits.

It was shown that it was necessary to incorporate not only the unequal reactivity of NCO group but also that of triols to account for the interesting observations made on geltime vs. NCO/OH ratio. It was shown that as R increases CO_2 evolved increases for a given $\bar{M}_w$. Also, as ρ increases the CO_2 evolved decreases.

If it is assumed that reactivity of an end group is unaffected by chain length and that second order kinetics apply, the following equations can be written.

$$-\frac{d[A]}{dt} = (k_1+k_2)[A]\{[B] + K[C] + K K_R[D]\} \tag{A1}$$

$$\frac{dA_1^r}{dt} = k_1 [A]\{[B] + K[C] + K K_R[D]\} \tag{A2}$$

$$\frac{dA_2^r}{dt} = k_2 [A]\{[B] + K[C] + K K_R[D]\} \tag{A3}$$

$$-\frac{d[A_1^*]}{dt} = -\frac{dA_2^r}{dt} + k_1^*[A_1^*]\{[B] + K[C] + K K_R[D]\} \tag{A4}$$

$$-\frac{d[A_2^*]}{dt} = -\frac{dA_1^r}{dt} + k_2^*[A_2^*]\{[B] + K[C] + K K_R[D]\} \tag{A5}$$

$$-\frac{d[C]}{dt} = K[C]\{(k_1+k_2)[A] + k_1^*[A_1^*] + k_2^*[A_2^*]\} \tag{A6}$$

$$-\frac{d[D]}{dt} = \frac{d[C]}{dt} + K K_R[D]\{(k_1+k_2)[A] + k_1^*[A_1^*] + k_2^*[A_2^*]\} \tag{A7}$$

$$-\frac{d[B]}{dt} = [B]\{(k_1+k_2)[A] + k_1^*[A_1^*] + k_2^*[A_2^*]\} \tag{A8}$$

Since initially only monomer is present, $A_1^r = A_2^r = 0$ initially[15]. Dividing (A3) by (A2) and integrating with the above initial condition

$$A_2^r = K_A A_1^r \tag{A9}$$

where $K_A = k_2/k_1$. Combining this with (16) and (17) it is easy to show that

$$\frac{x_2(1-x_1)}{x_1(1-x_2)} = K_A \tag{A10}$$

Initially $[A_1^*] = [A_2^*] = 0$ and these are the initial conditions for (A4) and (A5)[15]. Substituting (A3) into (A4) and dividing

the resulting equation by (A1),

$$\frac{d\,A_1^*}{d\,A} = -\frac{k_2}{k_1+k_2} + \frac{k_1^*}{k_1+k_2}\frac{[A_1^*]}{[A]}$$

The initial A_1A_2 monomer concentration is $[A]_o$. Hence the above can be integrated[15] with the condition that $[A_1^*] = 0$ when $[A] = [A]_o$. The result is

$$\frac{[A_1^*]}{[A]_o} = \frac{K_A}{K_1-1-K_A}\left[\frac{[A]}{[A]_o} - \left(\frac{[A]}{[A]_o}\right)^{\frac{K_1}{K_A+1}}\right] \tag{A11}$$

where $K_1 = k_1^*/k_1$. Similarly substituting (A2) into (A5), dividing by (A1) and integrating

$$\frac{[A_2^*]}{[A]_o} = \frac{1}{K_A K_2-K_A-1}\left[\frac{[A]}{[A]_o} - \left(\frac{[A]}{[A]_o}\right)^{\frac{K_A K_2}{K+1}}\right] \tag{A12}$$

where $K_2 = k_2^*/k_2$. These results are identical to those given in reference 15 and hence equations (20), (23) and (24) of that reference, reproduced below, are also valid

$$\mathcal{K} = \frac{[A]}{[A]_o} = \frac{1-x_1}{K_A x_1+1} = \frac{K_A(1-x_2)}{x_2 + K} \tag{A13}$$

$$1-x_1^* = \frac{K_A x_1 + 1}{x_1(K_1-1-K_A)}\left\{\frac{1-x_1}{K_A x_1+1} - \left(\frac{1-x_1}{K_A x_1+1}\right)^{\frac{K_1}{K_A+1}}\right\} \tag{A14}$$

$$1-x_2^* = \frac{K_A x_1 + 1}{x_1(K_A K_2-1-K_A)}\left\{\frac{1-x_1}{K_A x_1+1} - \left(\frac{1+x_1}{K_A x_1+1}\right)^{\frac{K_A K_2}{K_A+1}}\right\} \tag{A15}$$

The above can be easily obtained by combining (16) to (20) with (A9) to (A12). For the other groups, the initial conditions are $[C] = [C]_o$, $[D] = 0$ and $[B]=[B]_o = f[B_f]_o = 2 + [B_2]_o$. Dividing (A6) by (A8) and integrating after using (21) and (22)

$$(1 - \gamma) = (1 - \beta)^K \tag{A16}$$

Dividing (A7) by (A6) and integrating after using (22) and (23)

$$\xi = \gamma - \frac{1 - \gamma}{K_R - 1} \left[1 - (1 - \gamma)^{K_R - 1} \right] \tag{A17}$$

Substituting these relations in (24) and equating it to (30) it is easy to show that stoichiometric relation reduces to

$$\frac{\alpha_1}{K_A \alpha_1 + 1} \left[1 + \alpha_2^* + K_A(1 + \alpha_1^*) \right] = \frac{1}{R(1 - d)} \left[2\beta + (1 - d)(\gamma + \xi) \right]$$

which is (36).

Similarly it is easy to show that

$$P_{BB} = 4 \; \frac{\alpha_2^* + K_A \alpha_1^*}{1 + \alpha_2^* + K_A(1 + \alpha_1^*)} \quad \frac{d\beta^2}{2\beta + (1 - d - \beta)(\gamma + \xi)}$$

$$P_{CD} = 4 \; \frac{\alpha_2^* + K_A \alpha_1^*}{1 + \alpha_2^* + K_A(1 + \alpha_1^*)} \quad \frac{(1 - d - \beta)\delta}{2\beta + (1 - d - \beta)(\gamma + \xi)}$$

$$P_{Bf} = 4 \; \frac{\alpha_2^* + K_A \alpha_1^*}{(1 + \alpha_2^*) + K_A(1 + \alpha_1^*)} \quad \frac{\beta(1 - d)\beta}{2\beta + (1 - d - \beta)(\gamma + \xi)}$$

These relationships can be substituted into the gelation condition (34) to obtain (35). Further if any one probability is known the rest can be calculated for a given initial composition specified by R, β and d. For example if α_1 is known, α, α_1^* and α_2^* can be calculated by (A13), (A14) and (A15) respectively. γ and ξ are related to β and hence the stoichiometric relationship (36) can be used to obtain β. The value of α_1 at any time can be obtained by integration of (A2) as indicated earlier[12].

APPENDIX B

The complete set of reactions can be represented by the following equations:

$$- \frac{d[A]}{dt} = (k_1+k_2)[A]\left\{[B] + K[\bar{C}] + K\,K_R[D] + K_E[E] + K_F[F]\right\}$$

(B.1)

$$\frac{d[A_1^r]}{dt} = k_1[A] \qquad\qquad \left\{ \qquad\qquad \text{''} \qquad\qquad \right\}$$

(B.2)

$$\frac{d[A_2^r]}{dt} = k_2[A] \qquad\qquad \left\{ \qquad\qquad \text{''} \qquad\qquad \right\}$$

(B.3)

$$- \frac{d[A_1^*]}{dt} = - \frac{d[A_2^r]}{dt} + k_1^*[A_1^*] \left\{ \qquad \text{''} \qquad \right\}$$

(B.4)

$$- \frac{d[A_2^*]}{dt} = - \frac{d[A_1^r]}{dt} + k_2^*[A_2^*] \left\{ \qquad \text{''} \qquad \right\}$$

(B.5)

$$- \frac{d[C]}{dt} = \left\{(k_1+k_2)[A] + k_1^*[A_1^*] + k_2^*[A_2^*]\right\} K[C]$$

(B.6)

$$- \frac{d[D]}{dt} = \left\{ \qquad\qquad \text{''} \qquad\qquad \right\} K\,K_R\,D$$

(B.7)

$$- \frac{d[B]}{dt} = \left\{ \qquad\qquad \text{''} \qquad\qquad \right\} [B]$$

(B.8)

$$- \frac{d[E]}{dt} = - \left\{ \qquad\qquad \text{''} \qquad\right\}(B - K_E[E])$$

(B.9)

$$- \frac{d[F]}{dt} = \left\{ \qquad \text{''} \qquad\right\}(-KK_R[D] + K_F[F])$$

(B.10)

Using eqns. B1-B8 we obtain

$$1 - \gamma = (1-\beta)^K$$

(B.11)

$$\delta = \gamma - \frac{1-\gamma}{K_R - 1}\left[1 - (1-\gamma)^{K_R-1}\right]$$

(B.12)

The equations relating α_1^*, α_1^* and α_2^* are same as A14 and A15 of Appendix A.

From equations B9 and B8 we obtain

$$- \frac{d\,[E]}{d\,[B]} = 1 - K_E \frac{[E]}{[B]}$$

with boundary condition $[E] = 0$ when $[B] = B_o$ we obtain

$$\frac{[E]/B_o}{\{[B]/B_o\}^{K_E}} = \frac{1}{1-K_E}\left[\left(\frac{[B]}{B_o}\right)^{1-K_E} -1\right]$$

$$= \frac{1}{1-K_E}\left[(1-\beta)^{1-K_E} - 1\right] \tag{B.13}$$

or,

$$\beta - \epsilon = \frac{1}{1-K_E}\left[(1-\beta) - (1-\beta)^{K_E}\right]$$

or,

$$\epsilon = \beta - \frac{(1-\beta)}{(K_E - 1)}\left[1 - (1-\beta)^{K_E-1}\right] \tag{B.14}$$

From equations B10, B6 and B7 we obtain:

$$\frac{d\,[F]}{d\,(C)} = -\frac{d\,[D]}{d\,[C]} + \frac{[F]}{[C]}\left(\frac{K_F}{K}\right)$$

$$\frac{d\,[D]}{d\,(C)} = \frac{K_R}{K_R - 1}\left[1 - \left(\frac{[C]}{[C_o]}\right)^{K_R-1}\right]$$

for consumption of D only.

or,

$$\frac{d\,[F]}{d\,[C]} = \frac{[F]}{[C]}\left(\frac{K_F}{K}\right) - \frac{K_R}{K_R - 1}\left[1 - \left(\frac{[C]}{[C_o]}\right)^{K_R-1}\right]$$

Solving with boundary conditions $[F] = 0$ at $[C] = C_o$ we obtain

$$\frac{[F]/C_o}{\{[C]/C_o\}^{K_F}} = \frac{K_R}{K_R - 1}\left[\frac{1}{(1-K_F)} - \frac{1}{K_R - K_F}\right]$$

$$- \frac{K_R}{K_R - 1} \left[\frac{([C] / C_o)^{1 - K_F}}{1 - K_F} - \frac{([C] / C_o)^{K_R - K_F}}{K_R - K_F} \right]$$

Or,

$$\emptyset = \delta + \frac{K_R}{K_R - 1} \left[\frac{(1 - \gamma)^{K_F} - (1 - \gamma)}{K_F - 1} - \frac{(1 - \gamma)^{K_F} - (1 - \gamma)^{K_R}}{K_F - K_R} \right]$$

$$(B.15)$$

APPENDIX C

Macosko's[7] method was used to derive the equation for sol fraction and network density. The formulae derived are reproduced below. For brevity their derivation is not presented here

<u>Sol-fraction:</u>

For Model 1 (as in Chapter 2, $\rho = 1$)

$$w_s = \text{Sol fraction} = D1\ C^2 + D2\ C^2 + D3\ PA1\ PA2L$$
$$+ D4\ PA2\ PA1L + D5 \qquad (C1)$$

$$\alpha = (1 - \alpha_1)/(1 + K_A \alpha_1\ )$$

$$A = (\frac{1-d}{d}) - \frac{1}{d}\left[\frac{1 + \alpha_2^* + K_A\ (1 + \alpha_1^*)}{\alpha_2^{*2} + K_A \alpha_1^{*2} + 1 + K_A}\right]$$

$$B = \left[\frac{1 + \alpha_2^* + K_*\ (1 + \alpha_1^*)}{1 + K_A + \alpha_2^{*2} + K_A \alpha_1^{*2}} - \beta\right] /d$$

$$C = (-A + \sqrt{A^2 - 4AB})/2$$

$$D = dC^2 + (1 - \rho)C$$

$$PA1 = D$$

$$PA2 = D$$

$$PA2L = (1 - \alpha_2^*) + \alpha_2^* D = PA1L$$

$$DO = d\ M_{B_3}/3 + (1 - \rho)\ M_{B_2}/2 + RM_{A_2}/2$$

$$D1 = d\ M_{B_3}/3DO$$

$$D2 = (1 - \rho)\ M_{B_2}/ 2DO$$

$$D3 = \left(-\frac{R}{2}\cdot\right)\left(\frac{1-\alpha}{1+K_A}\right) M_{A_2}/DO$$

$$D4 = \left(-\frac{R}{2}\right)\left(\frac{1-\alpha}{1+K_A}\right) K_A M_{A_2}/DO$$

$$D5 = \left(-\frac{R}{2}\cdot\right)(\alpha) M_{A_2}/DO$$

Average molecular weight between branch points ($\bar{M}_C$)

For Model 1 (Chapter 2, No water)

$$\bar{M}_C = \beta\left[(2 M_B + M_A)\frac{P_{B_f}}{(1-P_{BB})} + (M_A + M_{B_2})\frac{P_{BB}\ P_{B_f}}{(1-P_{BB})^2}\right] \qquad (C2)$$

$$P_{B_f} = 2(1-d)\left[\frac{\alpha_2^* + K_A\alpha_1^*}{1+\alpha_2^* + K_A(1+\alpha_1^*)}\right]$$

$$P_{BB} = 2d\beta\left[\frac{\alpha_2^* + K_A\alpha_1^*}{1+\alpha_2^* + K_A(1+\alpha_1^*)}\right]$$

Network density was derived using Macosko's approach for Model 2 (Chapter 3) for the case of no water present.

$$\text{Network concentration} = [B_{f_0}]\Big[(1-F_B)^3 + 3\in(1-F_A)(1-F_B)^2$$

$$(3F_B-1+\beta) + \frac{6\in^2}{\beta}(1-F_B)(1-F_A^2)F_B(F_B-1+\beta)$$

$$+3(1-F_A)^3(F_B-1+\beta)^3\in^4/\beta^3\Big] \qquad (C3)$$

$$F_B = (1-\sqrt{1-4MN})/2M$$

$$F_A = B + (F_B^2\beta+\beta\in)\ C/(\beta+\in(1-C))$$

$$M = \beta C(\beta+\in)/(\beta+\in(1-C))$$

$$N = (1-\beta) + B_{f0T}\in)^2/(\beta+\in(1-C))$$

$$B = \frac{(1+K_A) - (\alpha_2^* + K_A\alpha_1^*)}{1+\alpha_2^* + K_A(1+\alpha_1^*)}$$

$$C = 2\frac{\alpha_2^* + K_A\alpha_1^*}{1+\alpha_2^* + K_A(1+\alpha_1^*)}$$

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